The Study of Complexation of Some Metal Ions in Complexing Media

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Certificate

Certified that *Shri S L. Agarwal, Lecturer in Chemistry, Bipin Bihari College, Jhansi,* a candidate for the Degree of Doctor of Philosophy in Chemistry of Bundelkhand University, Jhansi, has worked under my guidance and that the accompanying thesis, on *The Study of Complexation of Some Metal Ions in Complexing Media,* which he is submitting, is his own work.

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C O N T E N T S

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C H A P T E R - I.

General Introduction, Survey of Literature, Object and Scope of Proposed work.

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CHAPTER I

INTRODUCTION:

Upto the end of Nineteenth Century formation of certain compounds e.g., interaction of metal compounds (inorganic compounds) and organic substances could not be explained. However, the name complex compounds were given to these interacted compounds. Sidgwick, Ostwald, Werner etc.,[1-7] tried to explain the formation of these complexes but no fruitfull and explanatory conclusion could be made.

Later, in the year 1881 Werner[8] gave a theory to explain the formation and constitution of these compounds. This theory proved to be good enough important and even now a days it has significant application. The main postulates of the werner theory are as follows:-

I. Metal inaddition to primary valency possess a secondary valency or auxillary valency. The secondary valency is responsible for a combination of a metal with ligands even when its combining power is exhausted.

II. Every metal has a fix number of secondary valency and is known as Co-ordination Number.

III. Primary valencies are always satisfied by negative ion while secondary valencies may be satisfied either by negative ions or by neutral molecules. In every case the co-ordination number of a metal should be fulfilled.

IV. The secondary valencies are directed in the space about the central metal ion. If a metal has the co-ordination number 6, the secondary valencies will be directed to the six apices of a regular octahedron and the metal which has co-ordination number 4, the auxillary valency bound will be directed either towards the four corners of a regular tetrahedron or towards the four Corners of a square plane.

Lawry and Sugden[9] supported Werners' idea in the light of electronic theory of valency.

All the above theories are not completely applicable for a large number of complexes. Therefore, following three theories have been developed, recently, those are practically applicable to explain structures, stabilities and general properties of the complexes.

I. ELECTRO STATIC THEORY (CRYSTAL FIELD THEORY)

II. ATOMIC ORBITAL THEORY

III. MOLECULAR ORBITAL THEORY

STABILITY:

According to the electronic concept co-ordination compounds are formed as a result of Lewis, Acid-Base reaction, where the metal ion acts as an acid (or acceptor) and the ligands as the base (or donar). It can be concluded, therefore, that all the metals have got the tendency to form the co-ordination compounds. Whenever, metal ion and ligand interact to form a complex in solution state, there is always an equilibrium state. Thus, the equilibrium constant of metal ion and ligand's interaction can be determined. The stability constant is the reciprocal of equilibrium constant and it can also be determined. As the equilibrium constant is affected by certain factors, the stability constant is also affected. The stability constant depends on:

(1) Nature of the ligands co-ordinating,

(2) Nature of the metal ion,

(3) Temperature at which interaction is studied and

(4) Medium of interaction etc.

Sometimes, other factors e.g., concentration, substitution on the complexing agent, ionic strength etc., also influences the stability of complexes.

The transition metals are sub divided into two groups:

(a) Transition metals of 'd' sub-shell and

(b) Transition metals of 'f' sub-shell.

The elements from atomic number 21 to 30 (Sc to Zn), 39 to 48 (Y to Cd), 57 to 80 (La to Hg) except atomic number 58 to 71 (Ce to Lu) are known as transition element of 'd' sub-shell and the elements from atomic number 58 to 71 (Ce to Lu) and atomic number 90 and onwards (Th and onwards) are known as transition elements of 'f' sub-shell. The elements from 58 to 71 and 90 and onwards are also known as "inner transition elements" of '4f' and '5f' sub-shells respectively.

The inner transition elements have almost similar physical and chemical properties and have been placed in the III group and VI and VII period in the periodic-table. Since, the physical and chemical properties of inner transition elements are almost similar, until and unless very accurate and precious instruments are not used, the change in properties, constants, behaviour etc., can not be explained. However, the elements of 'd' sub-shell have wide difference in physical as well as in chemical properties and therefore, stability constant and other properties, can be studied more easily then to the inner transition elements.

As have already been discribed that the study of interaction of 'd' sub-shell transition metals with ligand is more easier than to the 'f' sub-shell transition metals. Thus, to choose any group of transition metals for interaction with the ligands will be more suitable, handy and benificial. Fe(II), Co(II), Ni(II) and Cu(II) are the transition metals of the first series i.e. from atomic number 21 to 30 (Sc to Zn), have atomic numbers from 26 to 29 respectively. Therefore, a large number of workers, chemists etc. had choosen these metals for interaction with the various types of ligands. The detailed periodic position of these metals is as follows:

PERIODIC POSITION

	III	IV	V	VI	VII	VIII	VIII	VIII	I	II
	d-block									
4th Pd.	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
5th Pd.	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
6th Pd.	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
7th Pd.	89● Ac	90 Th								

* 4f Sub-shell (Lanthanides)

● 5f Sub-shell (Actinides)

	Fe		Co		Ni		Cu	
Covalent Radii (in A° unit)	1.17	$\approx$	1.16	$\approx$	1.15	$\approx$	1.17	(Almost similar)
I Ionisation Potential (in electron volts)	7.9	$\approx$	7.9	$\approx$	7.6	$\approx$	7.7	(Almost similar)
Electro-negativity	1.8	$\approx$	1.8	$\approx$	1.8	$\approx$	1.9	(Almost similar)

As transition metals of 'd' sub-shell are very reactive with the ligands, there are certain points which should be taken into the consideration before choosing suitable ligands.

All these ligands which have elements like oxygen, sulphur, nitrogen, phosphorous, arsenic etc. are very good complexing agents because in these elements a lone-pair of electrons is available for interaction with the metal ion. On the basis of these points, a large number of workers have studied the interaction of Fe(II), Co(II), Ni(II) and Cu(II) metals with various ligands.

Shah & Patel[10] studied the interaction of Cu(II), Ni(II), Co(II) with 4- isonitroso -1- phenyl -3- methylpyrazoin -5- one. Complexes of Cu(II), Ni(II), Co(II) with N-benzoyl -L-valine, N-benzoyl glycyl -L- valine is ovaleric acid[11] saccharine[12] 4-amino- 3, 5, dimethyl isoxazole[13], hydantoin[14], N-methylimidazole[15], pyrrole -2- carboxaldehyde & β -alanine[16], 1-benzenesulfonamido -1, 2-bis (2'-benzimidazolyl) ethane[17], 2-hydroxy -1- naphthalidene-p-N-dimethylaniline[18], p-chlorobenzoyl acetone[19], 5-chloro-2- hydroxy -4-methylacetophenone oxime[20], biuret[21], nitroso-R-salt

(Disodium salt of 1-nitroso-2- naphthol 3, 6- disulphonic acid[22], 1-hydroxy -2 naphthoic, 2-hydroxy -1 naphthoic and O-phenoanthroline[23], 2-phenylaceto hydroxyamic acid[24], β -styrylphosphonic acid[25], 1-6, hexamethylenediamine - N,N,N'-N'-tetra methyl phosphonic acid [26], 1-amino -2- naphthol[27], 2-hydroxy -1- naphthaldehyde -4- phenyl -3- thiosemicarbazone[28], 2- hydroxy -5- methyl- acetophenone thiosemicarbazone[29], azoles (pentamethylene-tetrazole)[30], p-bromobenzoyl acetone[31], propionic, α and β - amino propionic acid[32], DL-3-amino -2- hydroxy propionic acid[33], 2,2' - bipiridyl and β -diketonates (2,2' - bipyridene and acetyl acetone, benzoyl acetone, dibenzoyl methane)[34], 2-hydroxy-1- naphthaldehyde-semicarbazone[35], 2- hydroxy -5- nitroacetophenone[36], N-benzoyl -p- tolyhydroxylamine[37], 5-chloro-2-hydroxy butyrophenone[38], N-salicylidene - β - alonine[39], 3-bromo salicylic acid[40], diphenylamine -2-2'-dicarboxylic acid[41], 2-pyridyl acetic acid[42], O-(N-α-methyl-2- hydroxy benzylideneimino) benzene sulphonic acid[43], 5-methylisoxazole[44], N-phenyl -2- thenoyl[45] are studied by different groups of workers.

The complexes of Cu(II), Co(II), Ni(II) and Fe(II) are studied by large number of workers, e.g. , aforesaid metal

complexes with -2- amino -5- (O-hydroxy phenyl) - 1, 3, 4 thiadiazole[46], 3-(N-2- furfuralideneimino) propionic acid[47], tridentate Schiff's Base N-(O-hydroxyphenyl)-5, 6-benzosalycilideneime[48], 1- carbamido -3- methylpyrozole -5- one[49], saccharic acid[50], substituted azobenzenes i.e. 4-hydroxy -3- formyl-azobenzene, 4-hydroxy-3- formyl-4-methyl azobenzene, 4-hydroxy -3- formyl 2- methyl azobenzene[51], orthohydroxy keto-anils i.e.; ethylenediamine anil of 2-hydroxy -5- methyl propiophenone, ethylenediamine anil of -2- hydroxy -5- methyl benzophenone, ethylenediamine of -2 hydroxy -5- chloro benzophenone[52], cynoacetyl salicyledene hydrazone[53], azelaic acid[54], 5-nitro salicylaldehyde, 5- chloro salicylaldehyde and 5-bromo salicylaldehyde[55], Schiff's Base of salicylaldehyde with aniline and its derivatives[56], 2-mercapto histamine[57], Schiff's Base of salicylaldehyde with p-aminophenol[58] are reported.

Several investigators had studied the interaction of these metals with different ligands not in the form of above group but they had taken either one metal or two metals for interaction at a time. This also indicates that these metals are very good complex forming metals but their

comparative properties are not taken into consideration by these workers. Complexes of Cu(II)only with different ligands are carried out by G.C. Herman etal., with 1- aza-4- thiopentane, 1, 7 -diaza -4- thiohepentane, 1, 10-diaza 4, 7-dithiadecane[59], by Giuseppe Arena etal; with O-phenylenediamine and mono, bi, tridentate carboxylic acid[60], by Y.K. Agarwal etal; with N-m-tolyl-p- methoxy benzohydroxamic acid[61] and N-O-tolylbenzohydroxamic acid[62], by Aleado Giriusti etal; with sulphamido & ethylenediamine[63], by M.M. Tananaiko etal; with diphenyl guonidine[64] by Isao Yoshida etal; with β-diketones[65], by Guiseppe Arena etal; mixed chelates with 2,2'-bi-pyridyl and malonic, succinic, phthalic, maleic acid[66] by G. Arena etal.

The mixed chelates of Cu(II) with bipyridyl and ethylenodiamino, histamine, Glycine[67] are also quoted in literature. Complexes of Cu(II) with mono-ethanolamine[68], 1,1,1-tris (aminomethyl) propane[69], 1-methyl-2- mercapto imidazole[70], 2-(-N-α-methyl-2- hydroxy benylideneimino) ethane-sulphonic acid[71], p-aminohipouric and rhodizenic acid[72], 2,2'- dipridyl and 8-mono and disubstituted malonic acid[73], N,N-di (2-hydroxy ethyl)- 1,3-propanediamine[74],

1,4,7-triazacyclodecane and 1,5,9-triazacyclododecane[75], 2-pyridine carboxaldehyde[76], 2,2'-dipyridyl and cyclohexane-1,1-dicarboxylic acid[77], 2,2'-dipyridyl and cyclopropone -1,1- dicarboxylic acid[78], salicyloyl hydrozide[79], phthalic acid[80], thiourea[81], 1,2-diaminobenzene oxalate and salicylate[82], protocatechuric acid[83], 2-(aminomethyl) -2-methyl -1,3-propane diamine[84], Fe(II)-chelates of carboxylic acid derivatives and piperazine[85], 2,2'-dipyridinium, diglycollic an iminodiacetic acid[86] are also reported in the literature.

The large groups of workers have carried out studies with Co(II) and Ni(II) and the complexes of these metals are widely reported in literature, e.g., the complexes of these metals with 2- methylthioethanol and 2-methylthioethane thiol[87], disalicylaldimine oxamide, di-(O-hydroxy acetophenone imine) oxamide, disaliylaldimine succinamide, di-(O-hydroxy acetophenone imine) succinamide[88], dimethyl aminoethanethiol[89], dihalobis (pyrazine)[90], glycine, 2-aminobutyric acid, 2-methylalanine and alanine[91], O-hydroxy acetophenone oxime and their derivatives[92], semicarbazone derived from salicylaldehyde and cinnamaldelyde with diphenyl ketone[93], Schiff's Bases of salicylidene -2- amino -4-

phenylthiazole, p-hydroxy benzylidene -2- amino -4- phenyl thiazole, p-hydroxy -m- methoxy benzylidene -2- amino -4- phenyl thiazole[94], different sulph drugs (sulpha pyridine, sulpha dimethoxime, sulpha methoxy pyridazine, sulpha phenozole)[95], 2,2- diphenyl acetohydroxamic acid[96], β-diketo arylazo compounds[97], N-salicylidene taurine[98], 2-hydroxy -5- nitropropiophenone oxime[99], methoxy and ethoxy acetates[100], pyridine[101], triethanolamine[102], thiosalicylic acid amide[103], -3- formyl -4- hydroxy -2- nitroazobenzene[104] are also available.

The Ni(II) complexes with histamine and histidine[105], furan -2- carboxylic acid[106], salicylaldelyde, O-hydroxy acetophenone, O-hydroxy propiophenone, O-hydroxy -5- methyl benzophenone[107], alanine[108], N,N, N',N'-tetra (2-hydroxy) ethylenediamine, 1,7-diaza -4- thiaheptane, 1,8-diaza -4- thiaoctane, 1,9-diaza -4- thiononane, 1,9-diaza -5- thiononane[110], β-diketones (acetylacetone, benzoylacetone, dibenzoylmethane, 2-thenoyl trifluoroacetone, dipivaloylmethane, -4- phenyl dibenzoyl methane, N-indole carboxymethane)[111], sulphamethazine salicylaldiamine[112],

sulphadimethoxin[113], 2- phenyl acetohydroxamic acid[114], 3-chloro -2- hydroxy butyrophenone[115], dipeptides[116], 2-2'- bipyridine[117], 5- methyltetrazole[118], 1-azo-4-thiapentane, 1,4-diaza-7- thiaoctane, 2-hydroxy ethyl thioethylamine[119], mono-ethanolamine[120], are studied by different workers.

Similarly complexes of Co(II) with Schiff's Bases of the type α-(C_5H_4N) C-Me = NNHCOR (where 'R' is phenyl, 2-thienyl, methyl radical)[121], O-2-pyrolidene imino benzoic acid[122], β -ethylthio ethylene thioglycollic acid[123], nicotine[124], 2,3-diamino propionic acid, 2,4-diamino butyric acid, lysine, arginine[125], 3-ethyl -4- methyl pyridine[126], meso-2,3-diamino butane- N,N'- disuccinic acid[127], are also reported in the literature.

So far complexes of Cu, Fe, Co, Ni with one ligand are discussed. Several workers have also carried out the interaction of these metals with more than one ligand i.e. mixed ligand. C. Arena etal., carried out interaction of Cu(II) with 2,2'-bipyridyl and malonic, succinic, phthalic, maleic acid[128], Cu(II) mixed chelates with bipyridyl and

ethylenediamine, histamine, glycine, malonic acid[129], 1,10-phenanthroline and citric, malic acid[130], Ni(II) mixed chelates with 1,10-phenanthroline/ 2,2'-bipyridyl and phenylamine[131], Cu(II) chelates with salicylic/ 5-sulphosalicylic acid and alanine, valine, α- aminobutyric, serine acid[132], 2,2'-bipyridine and 7-iodo-8-hydroxy quinoline -5- sulphonic acid (ferron)[133], 2,2'-dipyridyl and 8-mono and disubstituted malonic acids[134], Ni(II) chelates with imidazole and substituted O-hydroxy ketones[135], Cu(II) chelates with picolinic acid and β -phenyl alanine, α-alanine, glycine acid[136], Co(II) and Ni(II) with histidine and 2-phenyl aceto hydroxamic acid[137], Cu(II) and Ni(II) chelates with diethylene triaminepenta acetic acid (D.T.P.A.) and tiron[138], Ni(II) with 1,10-phenonthroline and catechol, proto-catechuic, thioglycollic, thiolactic and thiomalic acid[139] are also studied. B.D. Mali etal., studied the interaction of Cu(II) chelates with the two ligands both carboxylic acids, e.g., malonic acid as primary ligand and 5- sulphosalicylic, 3-5-dinitrosalicylic, 8-amino -1-naphthol-3, 6-disulphonic acid[140] as secondary ligand.

The interaction of metal ion with ligand to form complex compound can be studied in

1. solid state and
2. solution state.

In solid state the solid form of the complex is obtained by trial and error method with the help of change of pH, change of solvent etc. On the other hand the interaction of ligand and metal ion in solution state is studied by change of medium of interaction, ionic concentration, variation in temperature etc. In solid state properties of the complexes, structures can be easily studied by I.R. spectra, X-ray crystallography, magnetic suceptibility, Raman spectra, carbon, hydrogen and nitrogen estimation, chromatography etc. The study in solution state can be very easily and accurately be studied by pH-metric titration method. The other suitable methods include conductivity, polarography, spectrophotometery and potentiometery.

In solid state the structures of complex compounds by I.R. spectra are studied and are reported[46, 48, 62, 63, 87, 88, 90, 93, 94, 122, 141-143]. The study of complexation by X-ray diffraction method is studied by different group of workers[144-148]. In this method the study depends on the purity and crystal of the complex compound. As such the structure of the complexes by X-ray diffraction method are not so common.

Another important physical method for illustrating the properties of complexes is the measurement of the magnetic susceptibility. With the help of magnetic susceptibility the nature of complex viz., dimagnetism and paramagnetism can be decided. Bosco etal. studied Cu(II) and Ni(II) complexes with 2-methyl thioethanol and 2-methyl thioethane thiol[149], Alcado etal. studied Cu(II) and Ni(II) complexes with sulphamide and ethylenediamine[150], Antonio etal. studied the complexation of Cu(II) and Ni(II) with 2, 5-dimethyl- 1,3,4, - thiadiazole[151]. The complexes of Cu, Ni and Co with several ligands are also studied by maganetic susceptibility measurement by Narang and Lal[88], M. Goldstein etal.[90], Roy and Mohapatra[93] etc.

The study in solution state is mostly carried out by majority of workers because more usefull constants can be determined in this state. In this state stability const. (logk), change in enthalpy ($\triangle H$), change in free energy($\triangle G$), change in entropy ($\triangle S$), kinetics of the reaction, stoichiometry etc. can be determined. In this state the determination of above const. can also be studied by change in temperature, solvent, ionic strength i.e. the effect of temperature,

concentration, solvent can also be seen in this state . In this state conductivity measurement, pH-metry, polarography and spectrophotometry are mostly choosen by the workers. The author of this thesis with his colleage have also used this state for studying stability consts. and thermodynamic functions by pH-metric method. Beside determining the above consts., the effect of temperature and solvent on complexation are also shown and explained. The authors have choosen Cu, Ni, Co and Fe as metal ions and 2, 4, 6-trihydroxy acetophenone (phloro-acetophenone) as ligand and studied the interation in 50% water-ethanol/methanol medium at 25°C, 35°C, 45°C by pH-meter(152 and 153). R.C. Agarwal had studied the interaction of Th(IV) the ZrO(II) with this ligand by the pH-metric method(154). A large number of workers have studied the interaction of metal ion with the ligand by pH-metric method and some of them are as follows:

The interaction of Cu(II) with malonic, malic , succinic and phthalic acids were carried out by G. Arena etal.(155) and stability consts. of complexes are reported. A.P. Sakharov studied the interaction of Cu(II) with di and tri methylamine and found that the incwease of methyl group in the amines decreases the stability of the complexes(156).

S.K. Shrivastava studied the interaction of Cu and Ni with salicylaldehyde (SAL), O-hydroxy acetophenone (HAP), O-hydroxy propiophenone (HPP), O-hydroxy -5- methyl benzophenone (HMBP) in 75% dioxane-water medium and reported stability const. and thermodynamic functions. He also observed that the stability constant have the following relationship(157)

SAL < HAP < HPP < HMBP.

R.P. Singh etal. studied the interaction of Cu with 1-(2-pyridylazo) -2- phenanthol in 75% dioxan-water medium(158). Jahagirdar and Narwade studied interaction of Cu with 8-amino -1-naphthol-5, 7-disulphonic, 8-amino -1- naphthol -3. 6-disulphonic, 8-amino -1- naphthol -3, 5-disulphonic and 8-amino -1- naphthol -5- sulphonic acids(159). M. Santappa etal. studied the stability constant of Cu(II) with dipeptides viz; glycylglycine, glycyl -L- alanine, L- Alanyl-glycine, glycyl -L- leucine, leucyl-glycine(160). R.P. Agarwal studied the Cu(II) complexes with histidyl(161) histidine. K. Robert etal. studied Co(II) complexes with cystine and histidine(162). Adhikari and Hazara studied Cu and Ni complexes with hymato malonic acid(163). Mirnov, Sakurai

studied Fe, Co, Ni and Cu complexes with 2-mercapto histamine[164].

R.S. Sandhu and S.K. Kala found that stability constants of Cu, Ni, Co with N-benzoyl -L- valine, N-benzoyl glycyl -L- valine and isovaleric acid decreases with the rise of temperature[165]. In most of the cases when interaction in solution state is carried out and stability constants, so obtained, generally follow a definite order, which is known as Irving - Williams Rule[166-167]. R.C. Agarwal etal. have also found during interaction of Cu, Co, Ni, Fe with 5-sulphosalicylic acid[168] and thiosalicylic acid[169].

Thus the study in solution state by pH-metric method is very useful for showing effect of temperature, change of solvent change of ionic strength (μ) change in thermodynamic functions with temperature etc. Since many workers have used this method to acknowledge their contribution is not much useful and therefore acknowledgement of very few is under taken[16, 68,-71, 73, 86, 91,110, 123-126, 133, 135].

Another important method in solution state is

spectrophotometry. This method is only suitable for transition metals i.e., metals having coloured ions. As Cu, Ni, Co, Fe all have coloured ions, therefore, spectrophotometric method with these metal ions is suitable. Now a days this method is not so frequently choosen to study the interaction.

Object and Scope of the Proposed Work:

A survey of the existing literature on Cu, Ni, Co, Fe complexes reveals that in the past few years much interest has been shown in the study of interaction of these metals with the ligands. But very few have shown interest, so far, to show the effect of temperature and change of solvent on complexation. After going through literature it is found that no work is carried out so far with Cu, Ni, Co, Fe and 2, 4, 6 - trihydroxyacetophenone (phloroacetophenone).

As such in the present thesis the interaction of these metals with the proposed ligand (phloroacetophenone) at various temperature and different solvents is under taken. The solvents selected as medium of interaction are

1. Methanol,

2. Ethanol,

3. Iso-propanol

4. Dimethylformamide

5. Acetonitrile (methylcyanide)

The dielectric constant of these solvents are 32.6, 24.3, 18.3, 109.5, 37.5 respectively at 25°C[170]. In the present investigation an attempt will be made to show the effect of change of medium i.e., solvent (dielectric constant), effect of change in temperature and effect of metal ion i.e., whether the stability constants of metal ions are in concurrence with the Irving-William's Rule or not.

The investigation undertaken are compiled at one place in the form of present thesis to account some reasonable facts. The thesis is divided into the following chapters and subject matter.

<u>Chapter</u> I: General Introduction, Survey of literature, Object and Scope of Proposed Work.

<u>Chapter</u> II: Methods of determining the complex compound.

<u>Chapter</u> III: Preparation of ligand.

<u>Chapter</u> IV: Experimental (pH-metric measurements)

Chapter V : Results;

1. Computation of proton-ligand stability constant of ligand at various temperature and in different medium.

2. Computation of metal-ligand stability constant at various temperature and in different solvents.

3. Computation of change in free energy (ΔG) change in enthalpy (ΔH) and change in entropy (ΔS) of the complexes.

Chapter VI: Discussion.

Chapter VII: Conclusion.

Appendix : List of papers, published, accepted and communicated.

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C H A P T E R - II

Methods of Determining the Complex Compound.

CHAPTER II

Methods of Determining the Presence of Complex Formation:

Ley[1] concluded on the basis of the study of copper Glycinate that the chelates possess special properties and so behaved differently from the parent substance. Many such properties are used to show the presence of chelates. An important method, which a larger number of workers, have used is the isolation of the complex and its study. The method of isolation of complex causes sometimes some troubles, since the isolated product may also contain double salts, adsorbed ions of the metal and or ligand and molecules of the solvents etc. The removal of one of them may disturb the equilibrium[2]. Therefore, the study in the change of physico-chemical properties may provide reliable results for the complexes in solution without disturbing the equilibrium. The following are some of the most important methods used in the detection of complexes.

(1) Chemical methods:

Usually, the chemical behaviour of the metal changes during the complex formation e.g. when KCN is added to the $CuSO_4$ solution, a white precipitate is formed, which dissolves in the excess of KCN. At this stage the test for the copper

ions is not given by the solution due to formation of $Cu(CN)_2^{-}$ complex.

(2) Electrode potential method:

This method is used to investigate the complexes in solution. In this method the variation of concentration of one particular ion on the addition of complexing agent is determined with the help of E.M.F. measurements. The variation in the concentration is due to formation of the complex ions. The study by this method was first suggested by Bodlander[3] and Jaeques[4] and later on by Jeoffery[5]. Giorgio etal. studied Cu(II) mixed chelates of 1, 10-phenanthroline and citric/malic acid[6], Salvatore etal. studied Cu(II) mixed chelates of 2,2'- bipyridine and 7 - iodo -8- hydroxy quinoline - 5 - sulfonic acid (ferron)[7] by this method.

(3) Ion Exchange method:

The covalent linkage between a metal and a donor is characterised by low exchange rates with metal ion in solution. The low exchange rates, therefore, shows the existence of chelates in solution. Schubert and Linderbaum[8] studied a series of complexes by this method and also calculated the formation constants of the complexes.

(4) Colour of the solution:

The complex formation in many cases takes place with change in colour. Therefore, a change in colour on the addition of chelating agent to a metal ion indicates the presence of a chelate e.g., $Mn(CN)_2$ on reaction with KCN gives $K_4Mn(CN)_6$ a solid compound of dark blue colour.

(5) Freezing point method:

The depression in freezing point is directly proportional to the number of particles present in the solution. In complex formation the decrease in number of particles takes place, therefore, the depression in freezing point is also noted.

(6) X-Ray Crystallography:

This method gives a direct proof of the existence of the complex. In this method the experimental material used is in the crystalline form. Therefore, the X-Ray method is limited to a small number of substances. Few of the complexes studied by this method are quoted in literature[9-13].

(7) Polarography:

The reaction of metal ions at the dropping mercury electrode provides information which may be used for the

detection of complexes. This method has been used by various workers[14-16] for determination of step-wise formation constant of complexes. Gaur and Zutshi[17] and others[18] used this method for complexation study with rare-earth metals. R.P. Singh etal. used this method to study the complexation of Ni(II) and Cu(II) with 2, 3-dihydroxy pyridine and 2-amino -3- hydroxypyridine[19].

(8) Spectro-photometry:

The absorption of particular wave length depends on the structure of the complex. During the complex formation a change in structure takes place. Therefore, the spectro-photometric method for determination of complexation was very common but now a days it is not used frequently. By this method a number of rare earth complexes were studied[20-25]. Bonianin etal. studied interaction of Co(II), Ni(II) with 3-ethyl -4- methyl pyridine[26], Patel etal. studied the Cu(II), Ni(II), Co(II) and Zn(II) interaction with 2 - hydroxy -5- nitro acetophenone[27], Bhatt and Subramaniya studied the interaction of Ni(II) with triethanol amine[28] by spectrophotometer method.

Besides above, there are some other physical methods, they are :

(9) Infra-red spectra,(13, 29-39)

(10) Raman Spectra,

(11) Electronic Spectra,(13, 29-31, 35)

(12) Electron diffraction,

(13) Chromatography,

(14) Magnetic susceptibility,(13, 29-31, 35, 38)

(15) Conductivity(38) and

(16) pH-metry etc.

In the present investigation pH-metry has been utilised in the determination of composition, stability of complexes and change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) due to complex formation. The details of the method used are as follows:

pH metry:

All the metal-chelates may be considered as formed by the displacement of one or more usually weak acidic protons of the chelating agent by a metal ion. For example, the addition of aspartic acid to a solution of trivalent rare earth metal ion will follow, the following equilibrium as

studied by M.C. Agarwal[40] and Trivedi etal.[41]

$$M^{3+} + AspH_2 \longrightarrow M:AspH^{2+} + H^+.$$

Where, $M^{3+} \longrightarrow$ trivalent rare earth

$AspH_2 \longrightarrow$ Aspartic acid

$M:AspH^{2+} \longrightarrow$ Rare earth metal aspartate.

In the case of other transition metals i.e. those of d - subshells the probable equilibrium may be given by

$$M^{2+} + AspH_2 \longrightarrow M:AspH^{2+} + H^+$$

Where, $M^{2+} \longrightarrow$ divalent metal ion

Therefore, it may be concluded that the chelate formation of metal ions with ligand results liberation of protons (H^+). The liberated protons (H^+) are titrated with standard alkali solution and the change of pH is noted with the addition of alkali solution. The proton-ligand stability constant and the metal-ligand stability constant, (the complete details of calculation are explained some where else in forgoing chapter), are then calculated either by Calvin and Melchoir[42, 43] technique which is extension of Bjerrum's method[44] or by Irving-Rossotti technique[45-47]. The necessary correction is applied if the pH- titrations are carried out in the non-aqueous medimum as described by Van

Uitert and Haas[48].

The pH-metric method is very popular and common for the study of complex formation and is widely used. This method is good for the study with the transition metals as well as with the inner transition metals (rare earth). With this method stability constant, change in free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS) due to complexation can be determined. By the knowledge of these data the effect of temperature and/ or change of solvent, ionic strength can also be attributed. By using this method the aforesaid constants in aqueous and non-aqueous medium are reported by several workers. The stability constant and thermodynamic functions of Cu, Co, Ni and Fe, (some times one or two of these metals are taken for interaction only), with histanine and histamine[49]; furan -2- carboxylic acid[50]; 3 - (N-2- furfural indeneimino) propionic acid[51], mono ethanolamine[52], N.D. T.A.[53], alanine[54], azelaic acid[55], different derivatives of benzene sulphonic acid and ethane-sulphonic acid[56], 1 - aza -4- thiapentane, 1, 4- diaza -7- thiaoctone[57] are studied by different workers. A number of workers have also used this method with the rare earth metals

in aqueous and non-aqueous medium(58-72).

This method is also suitable for studying the interaction of metal ions in mixed ligands. The mixed ligand complexes of metals ($Fe(II)$, $Co(II)$, $Ni(II)$ and $Cu(II)$), for the present study are also reported in the literature(75-78).

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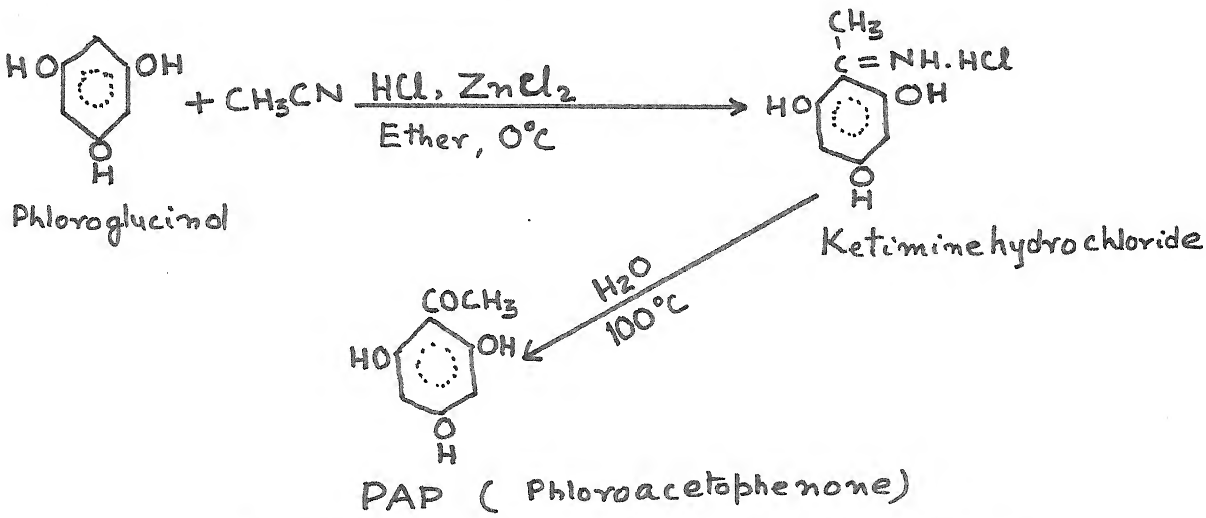
C H A P T E R - III

Preparation of Ligand

CHAPTER III

Preparation of 2, 4, 6 - trihydroxy acetophenone (Phloroacetophenone).

The 2, 4, 6 - trihydroxy acetophenone (phloroacetophenone, for the sake of convenience abbreviated as PAP) was prepared by Hoesch reaction (Houben-Hoesch reaction), an extension of Gattermann aldehyde reaction. The reaction can be illustrated as follows:



In actual preparation 20% by weight of dry phloroglucinol (25.2 gms.), 40% anhydrous acetonitrile (16.4 gms. or 20.9 ml.), 100 ml. of sodium dried ether and 5 gm. of finely powdered and fused zinc chloride ($ZnCl_2$) were taken and kept in ice salt mixture. The rapid stream of dry HCl gas was passed for two hours through the solution with continuous shaking. The flask containing the material was left

for 24 hours in ice chest and again stream of dry HCl gas was passed for another two hours. The flask was again left in ice chest for 72 hours. A bulky orange-yellow precipitate of kitimine-hydrochloride is formed. The excess ether was removed by decantation and the orange-yellow solid was washed by anhydrous ether. The solid was then transfered to a large round bottom flask, provided with the reflex condenser. The dissolved yellow solution was boiled for about two hours and then allowed to cool. When the cooling is allowed about 5 gm. activated charcoal was also added. The solution is again boiled for five minutes and filtered through a Buchner funnel under suction. The yellowish needle shaped structures of phloroacetophenone (PAP) was obtained[1-3].

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C H A P T E R - IV.

Experimental.

CHAPTER IV

EXPERIMENTAL:

The standard solutions of Fe(II), Co(II), Ni(II) and Cu(II) were prepared by dissolving $FeSO_4\ (NH_4)_2SO_4 \cdot 6H_2O$ (Ferrous ammonium sulphate), $Co(NO_3)_2$ (Cobalt nitrate), $NiSO_4$ (Nickel sulphate) and $CuSO_4 \cdot 5H_2O$ (Copper sulphate) in the double distilled conductivity water. All the solutions were prepared in acidic medium to prevent hydrolysis. However, the acid content in the metal solution were kept known.

The estimation of ferrous ion was carried out by using standard potassium dichromate solution[1]. The Co(II) was estimated gravimetrically by precipitating as cobalt-anthranilate from sodium anthranilate solution[2]. The estimation of Ni(II) was also carried out gravimetrically. The metal was precipitated by adding alcoholic solution of dimethylglyoxime, in a slightly hot and acidic solution, followed by excess of ammonium solution[3]. Copper (II) was estimated iodometrically by standard sodium thiosulphate solution[4].

The solution of PAP was prepared in 50% methanol,

ethanol, isopropanol, D.M.F. and acetonitril-water medium. All the solvents choosen as medium of interaction were distilled before use.

All the chemicals, stated above and sodium perchlorate NaOH, perchloric acid etc; used were BDH or equivalent.

pH-metric measurement:

As already discussed in previous chapters that the pH-metric method is very suitable to study proton-ligand stability constant, change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS). Therefore, this method is used to study above data. It is also very obvious from the chapter of introduction that pH-metric method is extensively used by a large group of workers.

In present investigations the Irving and Rossottii[5-8] technique were strictily followed. The pH-titrations were carried out in titration vessels (made of corning glass); through which the constant temperature water was circulated from thrmostat. The temperature of thermostat was electrically controlled to $\pm$ 0.1°C. In all the titrations the volume (50 ml.) and ionic strength (0.1M $NaClO_4$) were kept constant.

Though all the metals, used were divalent but their ionic valencies in anions (negatively charged ions) were different. Therefore, the following sets were prepared for pH-metric titrations.

__Set__ - __I__: 5ml. of 0.1M $HClO_4$ + 9.5ml of 1M $NaClO_4$ + 35.5ml of H_2O.

__Set__ - __II__: 5ml. of 0.1M $HClO_4$ + 9.0ml. of 1M $NaClO_4$ + 4ml. of o.125M PAP + 32 ml. of H_2O.

__Set__- __III__: 5ml. of 0.1M $HClO_4$ + 8.6 ml. of 1M $NaClO_4$ + 4 ml. of 0.125M PAP + 10ml. of 0.01 $CuSO_4$ + 22.4ml. of H_2O.

__Set__ - __IV__: 5ml.of 0.1M $HClO_4$ + 8.3ml. of 1M $NaClO_4$ + 4ml. of 0.125M PAP + 10ml. of 0.01M $FeSO_4(NH_4)_2SO_4$ + 22.7 ml. of H_2O.

__Set__ - __V__: 5ml. of 0.1M $HClO_4$ + 8.7ml. of 1M $NaClO_4$ + 4ml. of 0.125M PAP + 10ml. of 0.01M $Co(NO_3)_2$ + 22.3ml. of H_2O.

Set - VI: 5ml. of 0.1M $HClO_4$ + 8.7 ml. of 1M $NaClO_4$ + 4 ml. of 0.125M PAP + 10ml. of 0.01M $NiCl_2$ + 22.3 ml. of H_2O.

Since all the pH-titrations were carried out in different solvent-water medium (50% solvent-water mediums), the necessary corrections in pH-measurements were applied as given by Uitert and Haas[9].

The pH-measurements were carried out on a Systronix pH-meter (Model 322-1) with glass calomel electrodes. The pH-meter was standardised by using three different buffer solutions. The tables 1(a, b, c) to 5(a, b, c) show the change in pH of solution by addition of standard carbonate free[10] NaOH.

The observations in the above tables are plotted as shown in the figures 1 (a, b, c) to 5 (1, b, c).

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TABLE : I (a)

pH-metoric titrations at 25°C Methanol -H_2O system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml.of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.45	0.0	2.4	0.0	2.45	0.0	2.85	0.0	2.4	0.0	2.4
0.5	2.5	0.5	2.5	0.5	2.6	0.5	2.95	0.5	2.5	0.5	2.5
1.0	2.7	1.0	2.7	1.0	2.8	1.0	3.[illegible]	1.0	2.65	1.0	2.65
1.5	3.0	1.5	3.10	1.5	3.15	1.5	3.5	1.5	3.0	1.5	3.0
1.75	3.4	1.75	3.4	2.0	4.75	2.0	4.4	2.0	5.0	2.0	5.25
2.0	9.8	2.0	6.45	2.25	5.9	2.25	6.25	2.25	6.25	2.25	6.5
2.5	11.5	2.25	7.2	2.5	6.55	2.75	7.5	2.75	7.55	2.75	7.4
		2.5	7.6	2.75	7.1	3.25	8.0	3.25	7.95	3.00	7.85
		3.0	8.1	3.0	7.5	3.75	8.2	3.75	8.45	3.50	8.2
		3.5	8.75	3.5	8.05	4.0	8.7	4.00	8.75	4.0	8.9
		4.0	9.7	4.0	8.65	4.5	9.25	4.5	9.5	4.5	9.25
		4.5	10.25	4.5	9.7	5.0	9.75	5.0	10.1	5.0	10.1
		5.0	10.7	5.0	10.4	5.5	10.25	5.5	10.5	5.5	10.55

TABLE I V (B)

pH-meteric titrations at 35°C in 50% Methanol – H_2O system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml.of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.5	0.0	2.6	0.0	2.65	0.0	2.6	0.0	2.55	0.0	2.55
0.5	2.6	0.5	2.65	1.0	2.9	1.0	2.95	0.5	2.65	0.5	2.6
1.0	2.8	1.0	2.75	1.5	3.25	1.5	3.2	1.0	2.8	1.0	2.75
1.5	3.05	1.5	3.1	1.75	3.6	2.0	3.85	1.5	3.1	1.5	3.1
1.75	3.45	1.75	3.4	2.00	4.95	2.25	6.25	2.0	4.7	2.0	4.5
2.00	10.1	2.0	6.3	2.25	5.9	2.5	6.95	2.25	6.2	2.25	6.55
2.50	11.3	2.25	7.15	2.50	6.5	3.0	7.45	2.75	7.5	2.5	6.75
		2.5	7.55	2.75	7.1	3.5	7.84	3.00	7.9	3.5	7.8
		3.0	8.05	3.00	7.45	4.0	8.2	3.50	8.1	4.0	8.2
		3.5	8.7	3.50	8.00	4.5	8.7	4.00	8.4	4.5	8.65
		4.0	9.6	4.00	8.65	5.0	9.2	4.5	8.7	5.0	9.2
		4.5	10.2	4.50	9.6	5.50	9.75	5.0	9.45	5.5	9.8
				5.00	10.25	6.0	10.2	5.5	9.85		

TABLE : 1 (c)

pH-meteric titration at 45°C in 50% Methanol $-H_2O$ system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.6	0.0	2.6	0.0	2.7	0.0	2.8	0.0	2.7	0.0	2.7
0.5	2.7	1.0	2.9	1.0	3.0	1.0	3.05	1.0	2.95	1.0	2.95
1.0	2.85	1.5	3.2	1.5	3.[illegible]	1.5	3.35	1.5	3.25	1.5	3.25
1.25	3.00	1.75	3.55	1.75	3.65	2.0	4.25	1.75	3.6	1.75	3.6
1.50	3.2	2.0	6.45	2.00	4.6	2.30	5.95	2.00	4.75	2.0	4.6
1.75	3.55	2.25	7.25	2.25	5.55	2.75	7.15	2.25	5.75	2.25	5.6
2.00	9.5	2.50	7.55	2.5	6.30	3.00	7.35	2.5	6.75	2.5	6.65
2.25	10.85	2.75	7.8	2.75	7.05	3.50	7.75	3.00	7.85	3.0	7.85
2.5	11.15	3.00	8.05	3.00	7.4	4.00	8.15	3.50	8.15	3.5	8.2
		3.50	8.77	3.50	7.95	4.50	8.6	4.00	8.6	4.0	8.65
		4.00	9.6	4.0	8.55	5.00	9.15	4.50	9.4	4.5	8.45
		4.5	10.15	4.5	9.45	5.50	9.7	5.00	10.0	5.0	10.05
		5.0	10.55	5.00	10.15	6.00	10.15	5.5	10.5	5.5	10.5

TABLE : 2 (a)

pH-meteric titrations at 25°C in 50% Ethanol -H_2O system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml.of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	3.55	0.0	2.35	0.0	2.4	0.0	2.45	0.0	2.4	0.0	2.45
0.5	2.50	0.5	2.5	1.0	2.8	1.00	2.70	1.0	2.65	0.75	2.55
1.0	2.65	1.0	2.75	1.5	3.2	1.50	3.05	1.5	2.90	1.25	2.75
1.25	2.80	1.5	3.10	1.8	3.75	1.75	3.25	1.75	3.15	1.75	3.15
1.50	3.05	2.0	3.45	2.0	5.30	2.00	3.95	2.00	3.65	2.00	3.60
1.75	3.35	2.1	6.9	2.1	5.50	2.25	6.2	2.25	6.70	2.30	7.10
2.00	10.75	2.25	7.0	2.3	6.05	2.50	6.75	2.50	7.50	2.50	7.50
2.25	11.4	2.50	7.45	2.4	6.6	2.75	6.90	2.75	7.80	2.75	7.80
		3.00	7.8	2.7	7.2	3.00	7.6	3.00	8.00	3.25	8.15
		3.50	8.5	2.8	7.45	4.00	8.5	3.25	8.20	3.75	8.45
		4.00	9.05	3.0	7.80	4.50	8.90	3.75	6.45	4.25	9.00
		4.50	10.00	3.50	8.30	5.00	9.50	4.25	9.00	4.75	9.85
		5.00	10.6	4.00	8.95	5.50	10.25	4.75	9.80	5.25	10.45
				4.50	10.5	6.00	10.60	5.25	10.40		

TABLE I 2 (b)

pH-meteric titrations at 35°C in 50% Ethanol $-H_2O$ system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.6	0.0	2.5	0.0	2.6	0.0	2.6	0.0	2.5	0.0	2.5
0.5	2.7	1.0	2.8	1.0	2.9	1.0	2.85	0.5	2.6	0.5	2.7
1.0	2.85	1.55	3.2	1.5	3.2	1.5	3.15	1.0	2.75	1.0	2.8
1.25	3.00	1.75	3.55	1.75	3.55	2.0	3.8	1.75	3.10	1.75	3.15
1.5	3.25	2.00	6.85	2.00	4.75	2.25	6.15	2.25	6.4	2.25	6.55
1.75	3.50	2.30	7.55	2.25	5.85	2.50	6.8	2.5	7.3	2.5	7.35
2.00	10.50	2.5	7.85	2.50	6.40	2.75	7.25	2.75	7.65	2.75	7.65
2.25	11.1	3.0	8.3	2.75	7.2	3.00	7.55	3.25	8.00	3.25	8.05
		3.5	9.0	3.0	7.6	3.5	8.00	3.75	8.4	3.75	8.4
		4.0	9.95	3.5	8.2	4.0	8.4	4.25	8.75	4.25	8.9
		4.5	10.45	4.0	8.85	4.5	8.9	4.75	9.55	4.75	9.75
		5.0	10.9	4.5	9.8	5.0	9.4	5.25	10.2	5.25	10.35
				5.0	10.45	5.5	10.0	5.75	10.65	5.75	10.75

TABLE : 2 (e)

pH-Meteric titrations at 45°C in 50% Ethanol -H_2O system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.75	0.0	2.65	0.0	2.75	0.0	2.8	0.0	2.8	0.0	2.65
0.5	2.85	0.5	2.75	1.0	3.0	1.0	3.0	0.5	2.9	1.0	3.0
1.0	3.05	1.0	2.95	1.5	3.3	1.5	3.3	1.0	3.05	1.5	3.3
1.5	3.55	1.5	3.25	2.0	4.6	2.0	3.9	1.75	3.25	1.75	3.45
1.75	3.6	2.0	6.7	2.25	5.7	2.25	5.95	2.25	6.2	2.0	3.65
2.0	10.25	2.25	7.45	2.5	6.25	2.5	6.30	2.50	7.2	2.25	6.4
2.5	11.4	2.5	7.7	2.75	7.05	3.0	7.4	3.25	7.9	2.5	7.3
		3.0	8.20	3.0	7.55	3.5	7.9	3.75	8.2	3.00	7.75
		3.5	8.85	3.5	8.05	4.0	8.25	4.75	9.35	3.5	8.05
		4.0	9.8	4.0	8.65	4.5	8.7	5.0	10.00	4.0	8.45
		4.5	10.35	4.5	9.55	5.0	9.25	5.5	10.45	4.5	9.00
		5.0	10.75	5.0	10.25	5.5	9.85	6.0	10.9	5.0	9.75

TABLE : 3 (a)

pH-meteric titrations at 25°C in 50% Iso-propanol -H_2O system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.35	0.0	2.50	0.0	2.55	0.0	2.60	0.0	2.60	0.0	2.55
0.5	2.50	0.5	2.60	0.5	2.60	1.0	2.85	0.5	2.65	1.0	2.85
1.0	2.75	1.0	2.75	1.0	2.75	1.5	3.10	1.0	2.80	1.5	3.05
1.5	3.60	1.5	3.00	1.5	3.10	2.0	3.55	1.5	3.05	2.0	4.20
2.0	9.10	2.0	5.20	2.0	4.30	2.5	5.85	2.0	4.50	2.5	5.50
2.5	12.00	2.5	8.10	2.5	5.65	3.0	7.65	2.5	5.90	3.0	7.90
		3.0	8.60	3.0	7.25	3.5	8.20	3.0	7.70	3.5	8.55
		3.5	9.25	3.5	8.20	4.0	8.65	3.5	8.55	4.0	9.05
		4.0	10.30	4.0	8.65	4.5	9.05	4.0	9.10	4.5	9.90
				4.5	9.40	5.0	9.60	4.5	10.00	5.0	10.60
				5.0	10.40	5.5	10.25	5.5	10.80		

TABLE : 3 (b)

pH-metric titrations at 35°C in 50% Iso-propanol $-H_2O$ system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.60	0.0	2.65	0.0	2.75	0.0	2.60	0.0	2.60	0.0	2.70
0.5	2.70	1.0	2.90	1.0	3.00	1.0	3.00	1.0	2.95	1.0	2.95
1.0	2.95	1.5	3.20	2.0	4.40	2.0	4.00	2.0	4.20	2.0	4.10
1.5	3.40	2.0	5.60	2.5	5.75	2.5	5.50	2.5	5.60	2.5	5.65
2.0	8.85	2.5	7.60	3.0	7.10	3.0	7.60	3.0	7.75	3.25	8.00
2.5	11.70	3.0	8.50	3.5	8.10	3.5	8.00	3.5	8.60	3.5	8.45
		3.5	9.20	4.0	8.55	4.0	8.55	4.0	8.95	4.0	8.90
		4.0	10.15	4.5	9.25	4.5	8.90	4.5	9.90	4.5	9.95
		4.5	10.70	5.0	10.25	5.0	9.45	5.0	10.55		
						5.5	10.10				

TABLE : 3 (e)

pH-metric titrations at 45°C in 50% Iso-propanol -H_2O system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.60	0.0	2.75	0.0	2.75	0.0	2.85	0.0	2.80	0.0	2.75
0.5	2.80	1.0	2.90	1.0	3.05	1.0	3.10	1.0	3.05	1.0	3.05
1.0	2.95	2.0	6.15	2.0	4.50	2.0	3.70	2.0	3.95	2.0	3.90
1.5	3.20	2.5	7.90	2.5	5.75	2.5	5.85	2.5	6.00	2.5	5.70
2.0	6.60	3.0	8.40	3.0	7.00	3.0	7.55	3.0	6.70	3.0	7.10
2.5	11.50	3.5	9.05	3.5	7.95	3.5	8.10	3.5	8.40	3.5	8.25
		4.0	10.00	4.0	8.45	4.0	8.45	4.0	8.90	4.0	8.75
		4.5	10.55	4.5	9.20	4.5	8.95	4.5	9.85	4.5	9.25
				5.0	10.15	5.0	9.40	5.0	10.45	5.0	9.95
						5.5	10.25				

pH-meteric titrations at 25°C in 50% DMF $-H_2O$ system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.95	0.0	2.95	0.0	2.15	0.0	3.00	0.0	3.00	0.0	2.95
0.5	3.05	0.5	3.05	0.5	3.30	0.5	3.25	0.5	3.25	0.5	3.30
1.0	3.35	1.0	3.35	1.5	3.65	1.0	3.30	1.0	3.40	1.0	3.55
1.5	3.75	1.5	3.65	1.75	3.85	2.0	4.25	2.0	4.35	2.0	4.40
2.0	7.50	2.0	4.30	2.0	4.20	2.25	4.75	2.5	5.50	3.0	6.90
2.5	10.85	2.5	6.95	2.75	5.90	2.5	5.50	3.25	7.45	3.5	7.60
3.0	11.90	3.0	7.90	3.25	7.25	3.0	7.25	3.5	7.95	4.0	7.90
		3.5	8.45	3.5	7.80	3.25	7.50	3.75	8.40	4.5	8.50
		4.0	8.90	4.0	8.40	3.5	7.85	4.0	8.70	5.0	8.80
		4.5	9.75	4.5	8.80	3.75	8.00	4.5	9.00	5.25	8.95
		5.0	10.50	5.5	9.5	4.25	8.40	5.0	9.25		
						4.5	8.60				
						5.0	9.20				
						5.5	9.60				

TABLE : 4 (b)

pH-meteric titrations at 35°C in 50% DMF $-H_2O$ system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml.of NaOH	pH	ml. of NaOH	pH
0.0	3.00	0.0	3.00	0.0	3.10	0.0	3.15	0.0	3.35	0.0	3.05
0.5	3.15	0.5	3.10	0.5	3.25	0.5	3.30	0.5	3.20	0.5	3.15
1.0	3.35	1.0	3.35	1.0	3.50	1.0	3.60	1.0	3.30	1.5	3.65
1.5	4.20	1.75	4.25	1.75	4.25	1.75	4.15	1.5	4.50	2.0	4.50
2.0	7.30	2.25	6.90	2.25	5.60	2.25	5.20	2.0	4.50	2.0	4.50
2.25	10.00	2.5	7.95	2.5	6.80	2.5	6.55	2.5	7.00	2.5	7.00
2.5	10.80	3.0	8.45	3.0	7.75	3.0	7.65	3.0	7.95	3.0	7.80
		3.5	8.95	3.5	8.30	3.5	8.15	3.5	8.30	3.5	8.20
		4.0	9.80	4.0	8.80	4.0	8.50	4.0	8.50	4.0	8.55
		4.5	10.45	4.5	9.60	4.5	8.85	4.5	8.95	4.5	8.95
				5.0	10.40	5.0	9.50	5.0	10.30	5.0	10.20

TABLE : 4 (e)

pH-meteric titrations at 45°C in 50% DMF -H_2O system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	3.00	0.0	3.00	0.0	3.05	0.0	3.15	0.0	3.00	0.0	3.05
0.5	3.05	0.5	3.05	0.5	3.20	0.5	3.30	0.5	3.10	0.5	3.15
1.0	3.25	1.0	3.25	1.0	3.45	1.0	3.65	1.0	3.60	1.5	3.40
1.25	3.45	1.5	3.85	1.5	3.85	2.0	4.50	1.75	4.25	1.75	4.10
1.5	3.90	2.25	6.80	2.25	5.50	2.25	5.20	2.5	6.80	2.5	6.80
1.75	4.90	2.5	7.95	2.5	6.70	2.5	6.95	3.0	7.85	2.75	7.45
2.0	7.05	3.0	8.40	2.75	7.30	2.75	7.30	3.5	8.20	3.0	7.80
2.25	10.00	3.5	8.90	3.0	7.70	3.0	7.60	4.0	8.50	3.5	8.40
2.5	10.90	4.0	9.75	3.5	8.20	3.5	8.00	4.5	8.85	4.0	8.85
		4.5	10.45	4.0	8.70	4.0	8.45	5.0	9.55	4.5	9.25
				4.5	9.45	4.5	8.80			5.0	10.20

TABLE : 5 (a)

pH-metric titrations at 25°C in 50% Acetonitrile -H_2O system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.05	0.0	2.15	0.0	2.10	0.0	2.05	0.0	2.10	0.0	2.05
0.5	2.15	0.5	2.20	0.5	2.30	0.5	2.25	0.5	2.20	0.5	2.20
1.0	2.45	1.0	2.40	1.0	2.50	1.0	2.50	1.0	2.40	1.0	2.40
1.5	2.70	1.75	2.90	1.75	2.85	1.75	2.90	1.75	2.75	1.75	2.70
2.0	7.30	2.00	4.00	2.25	4.55	2.0	3.65	2.0	3.45	2.50	6.70
2.25	10.25	2.25	6.85	2.5	6.05	2.25	4.85	2.5	6.90	3.0	7.05
2.5	11.45	2.75	7.80	3.0	7.80	3.0	7.65	3.0	7.85	3.5	8.10
		3.25	8.35	3.5	8.30	3.5	7.95	3.5	8.15	4.0	8.45
		3.75	8.85	4.0	8.80	4.0	8.15	4.0	8.45	4.5	8.85
		4.25	9.65	4.5	9.15	4.5	8.50	4.5	8.65	5.0	9.55
		4.75	10.25	5.0	9.50	5.0	9.00	5.0	9.15		

TABLE : 5 (b)

pH-meteric titrations at 35°C in 50% Acetonitrile –H_2O system.

Set I ml. of NaOH	Set I pH	Set II ml. of NaOH	Set II pH	Set III ml. of NaOH	Set III pH	Set IV ml. of NaOH	Set IV pH	Set V ml. of NaOH	Set V pH	Set VI ml. of NaOH	Set VI pH
0.0	2.00	0.0	2.30	0.0	2.30	0.0	2.45	0.0	2.30	0.0	2.40
0.5	2.15	0.5	2.40	0.5	2.45	0.5	2.55	0.5	2.45	0.5	2.45
1.0	2.35	1.0	2.50	1.0	2.65	1.0	2.75	1.0	2.50	1.0	2.55
1.5	2.80	1.5	2.80	1.75	3.05	1.75	3.05	1.5	2.85	1.5	2.90
2.0	7.40	1.75	3.55	2.0	4.00	2.0	3.95	2.0	4.05	2.0	3.90
2.5	11.70	2.5	7.55	2.25	5.20	2.5	6.85	2.5	6.90	2.5	6.80
		3.0	8.35	2.5	6.40	3.0	7.60	3.0	7.75	3.0	7.70
		3.5	8.80	3.0	7.80	3.5	8.00	3.5	8.10	3.5	8.05
		4.0	9.60	3.5	8.25	4.0	8.40	4.0	8.40	4.0	8.35
		4.5	10.20	4.0	8.80	4.5	8.75	4.5	8.80	4.5	9.25
				4.5	9.60	5.0	9.20	5.0	9.55	5.0	9.40

TABLE I 5 (a)

pH-meteric titrations at 45°C in 50% Acetonitrile $-H_2O$ system.

Set I		Set II		Set III		Set IV		Set V		Set VI	
ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH	ml. of NaOH	pH
0.0	2.35	0.0	2.30	0.0	2.50	0.0	2.60	0.0	2.45	0.0	2.50
0.5	2.45	0.5	2.40	0.5	2.50	0.5	2.70	0.5	2.55	0.5	2.60
1.0	2.60	1.0	2.60	1.0	2.75	1.0	2.90	1.0	2.75	1.0	2.80
1.5	2.90	1.5	2.95	1.5	3.10	1.5	3.20	1.5	3.05	1.5	3.10
2.0	7.25	2.25	6.95	2.0	4.25	2.0	3.85	2.0	4.05	2.25	5.05
2.25	10.40	2.5	7.85	2.5	6.25	2.5	6.75	2.5	6.85	2.75	7.50
2.5	11.40	3.0	8.35	3.0	7.70	3.0	7.55	3.0	7.70	3.25	7.80
		3.5	8.90	3.5	8.15	3.5	8.00	3.5	7.95	3.75	8.40
		4.0	9.50	4.0	8.70	4.0	8.30	4.0	8.35	4.0	8.65
		4.5	10.00	4.5	9.50	4.5	8.65	4.5	8.90	4.5	9.05
		5.0	10.60	5.0	10.10	5.0	9.10	5.0	9.25	5.0	9.35

FIG. 1 (a)

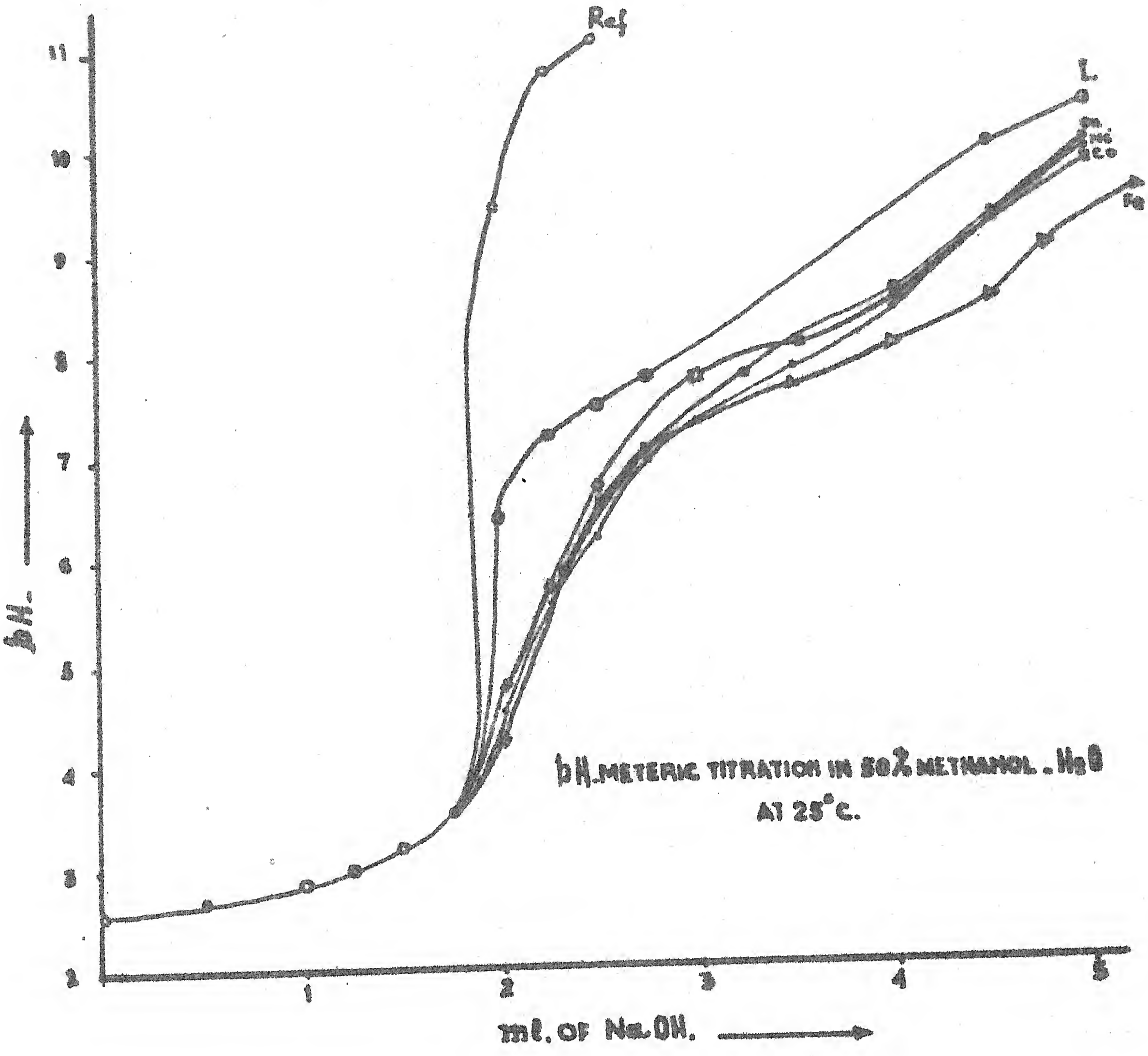
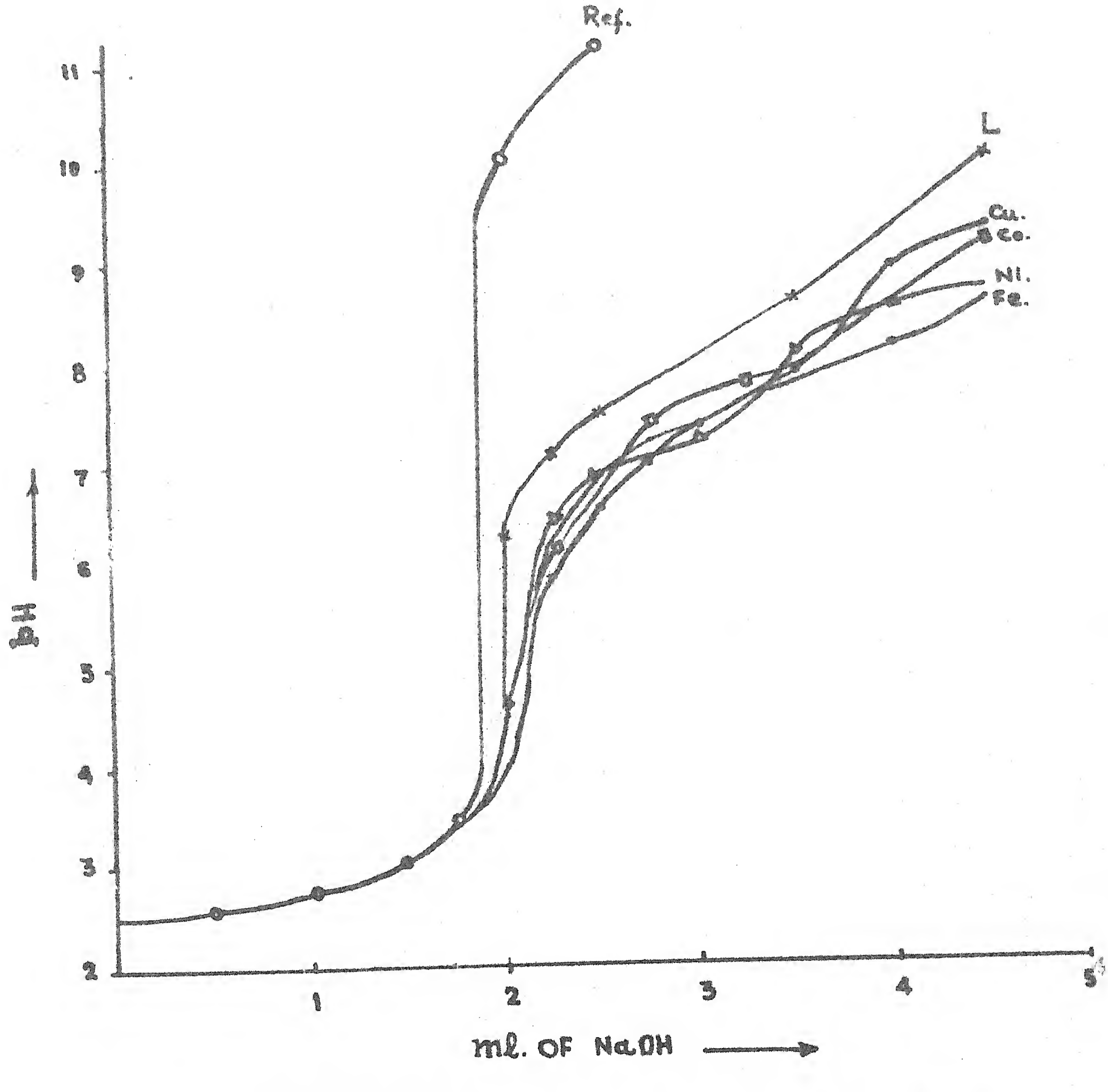

Ref
L
Cu
Ni
Co
Fe
pH.
ml. OF Na OH.
pH.METERIC TITRATION IN 50% METHANOL - H₂O
AT 25°C.

FIG_1(b)



pH-METERIC TITRATION IN 50% METHANOL-H_2O at 35°C.

FIG. 1 (C)

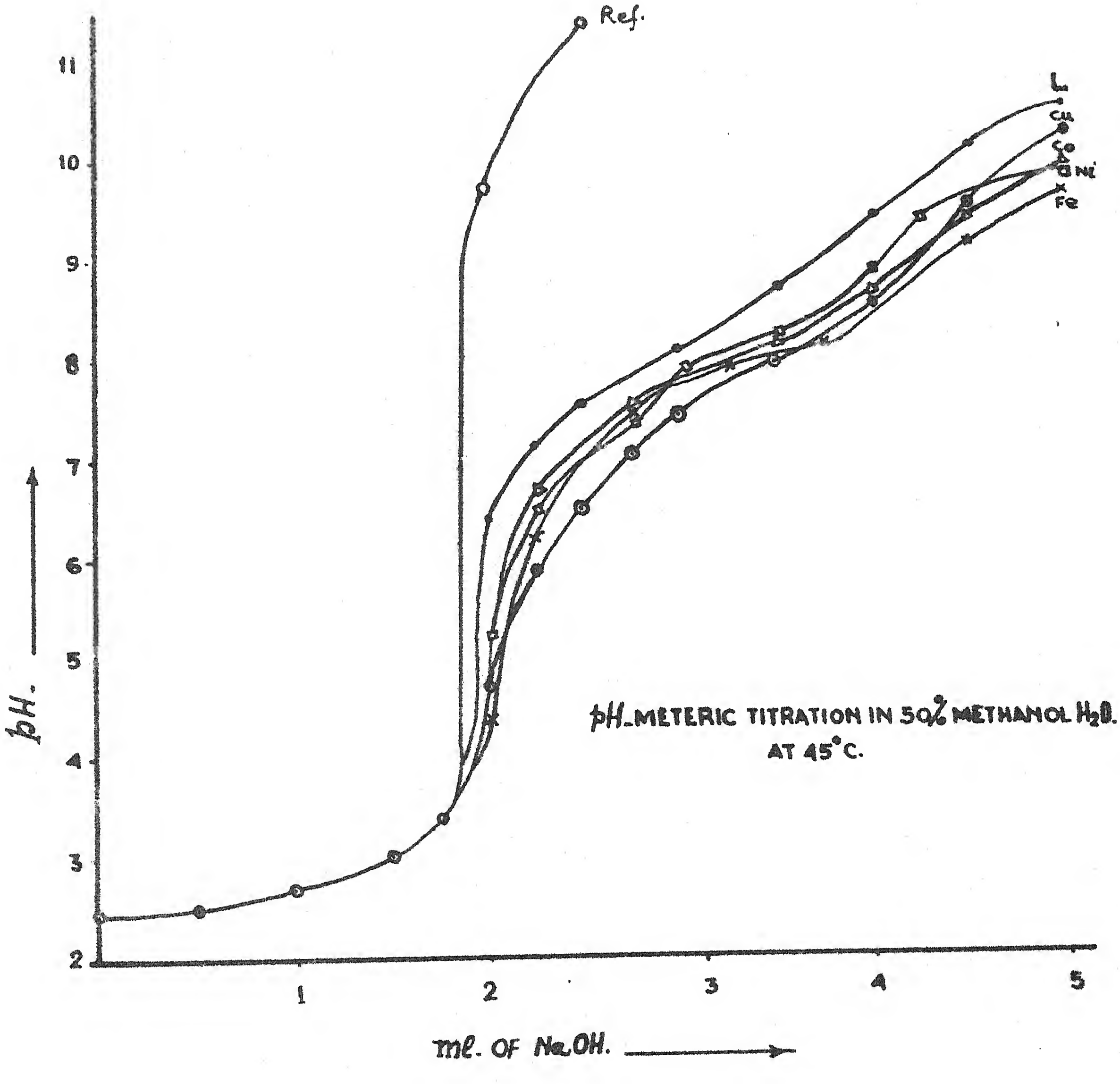
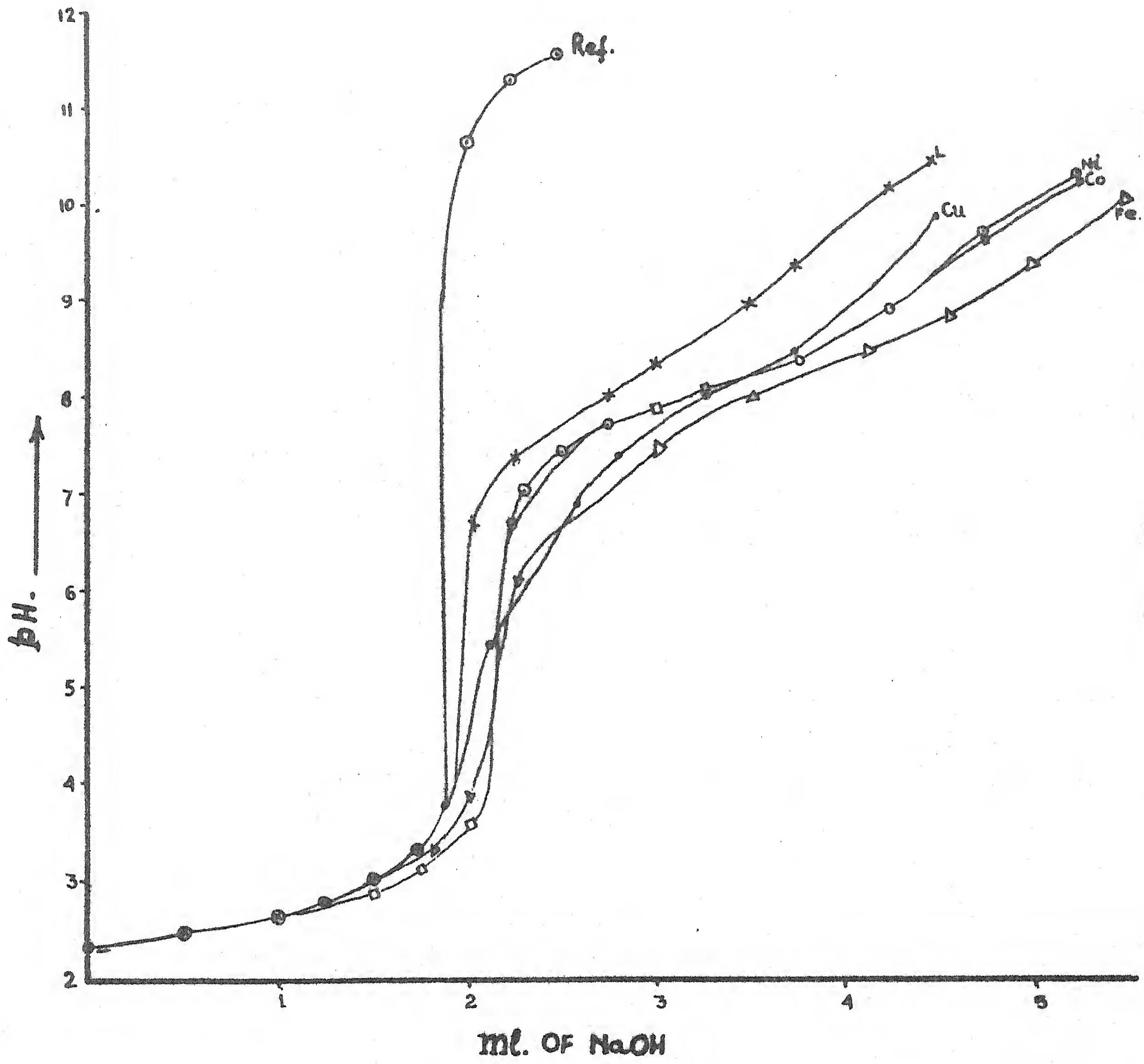
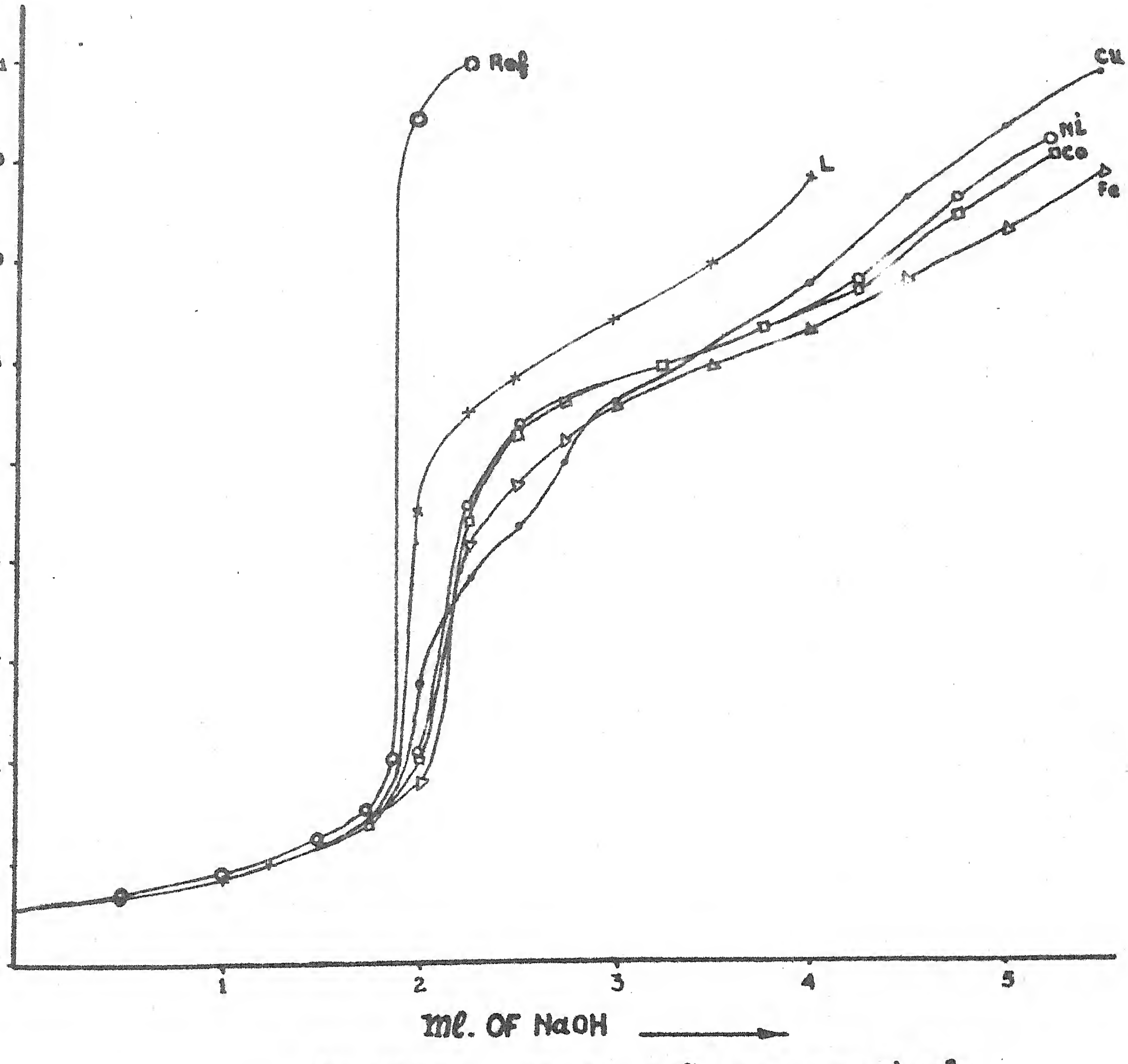

Ref.
L
Cu
Co
Ni
Fe
pH-METERIC TITRATION IN 50% METHANOL H2O.
AT 45°C.
pH.
ml. OF NaOH.
2
3
4
5
6
7
8
9
10
11
1
2
3
4
5

FIG_2 (a)



pH METERIC TITRATION IN 50% ETHANOL-H_2O at 25°c.

FIG. 2 (b)



pH. METERIC TITRATION IN 50% ETHNOL H2O at 35°C.

FIG.2 (C)

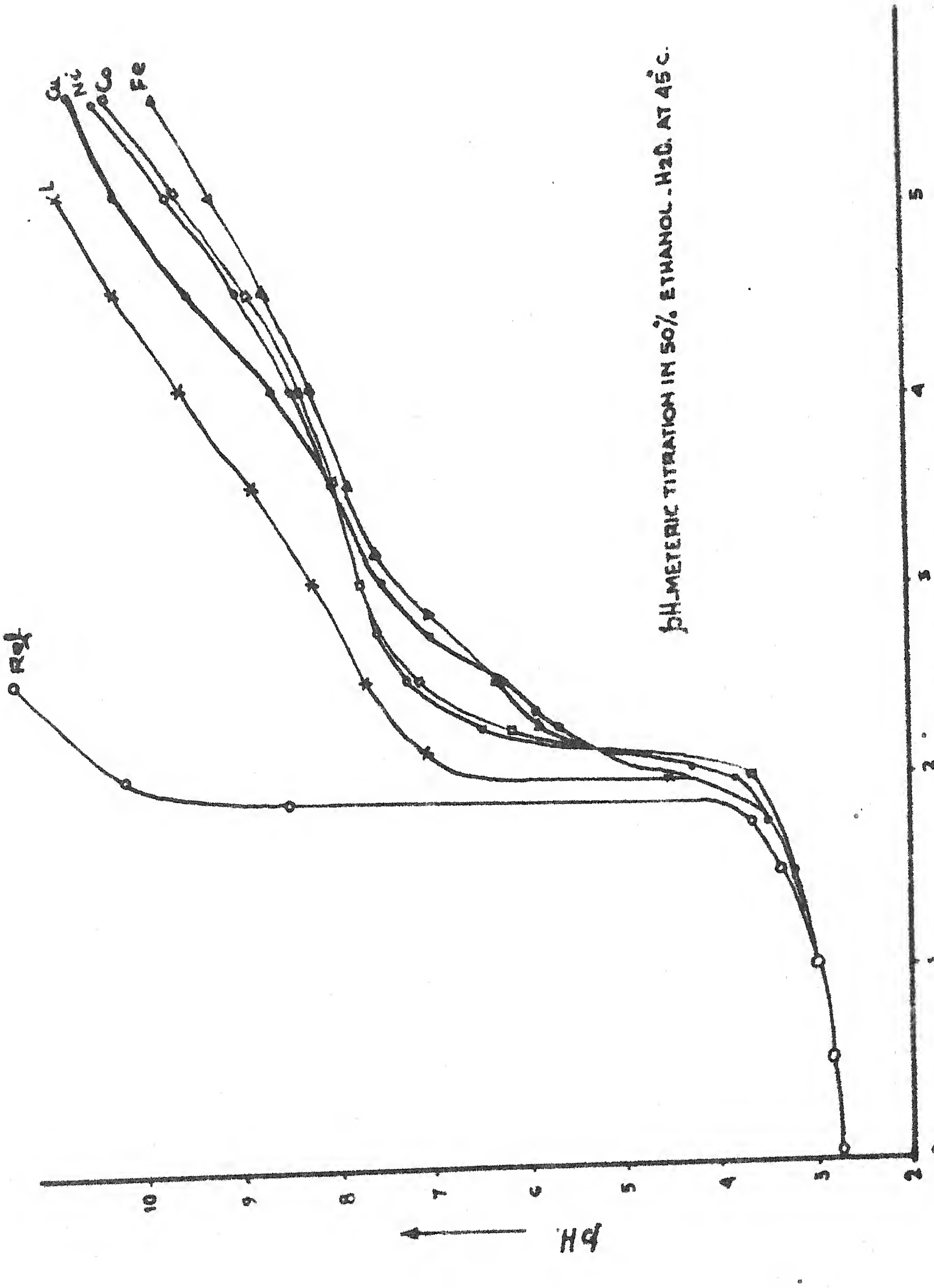
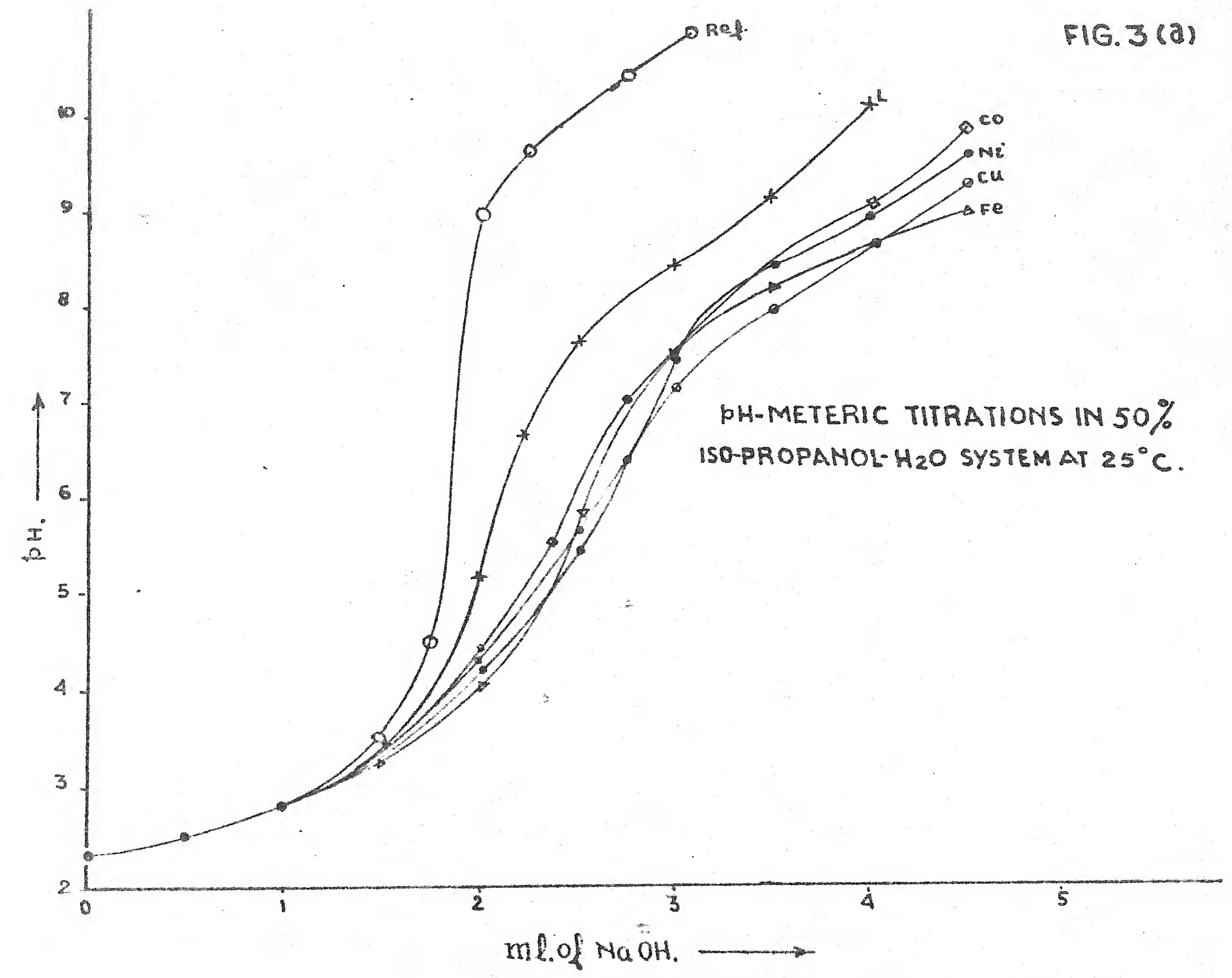
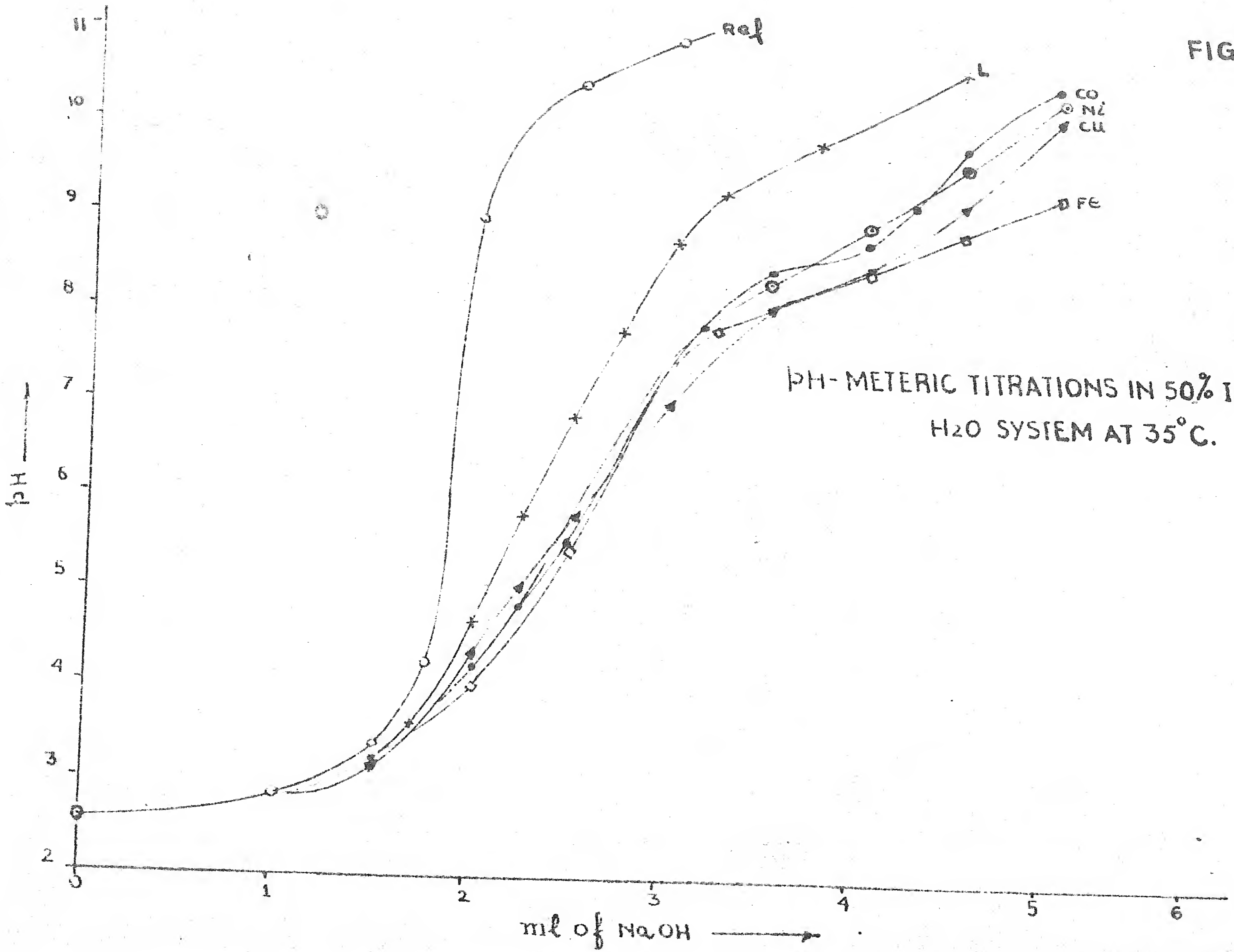

pH-METERIC TITRATION IN 50% ETHANOL-H2O AT 45°C.
Ref
L
Cu
Ni
Co
Fe
pH
ml OF NaOH
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5

FIG. 3 (a)



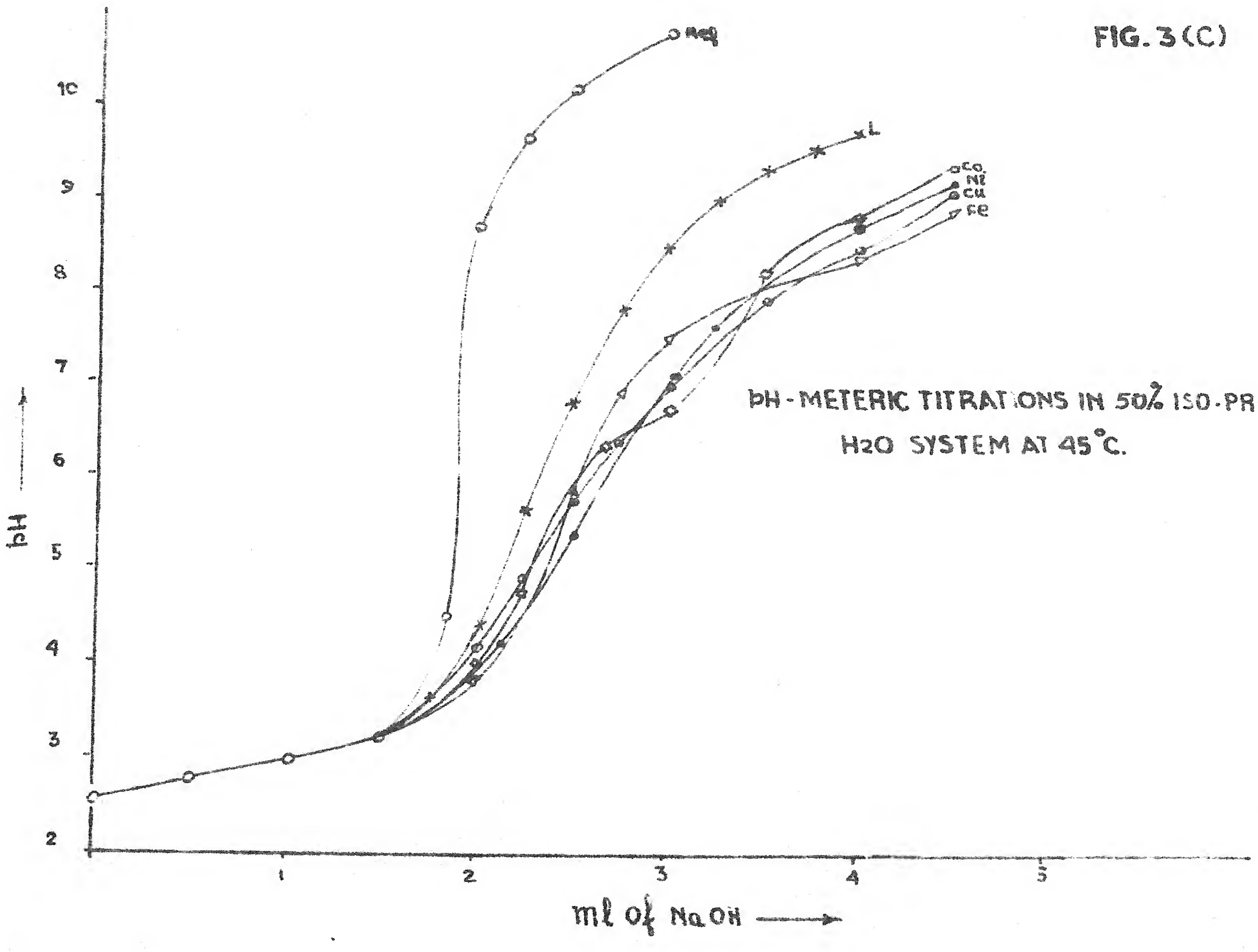
pH-METERIC TITRATIONS IN 50% ISO-PROPANOL-H_2O SYSTEM AT 25°C.

FIG. 3 (b)



pH-METERIC TITRATIONS IN 50% ISO-PROPANOL-H_2O SYSTEM AT 35°C.

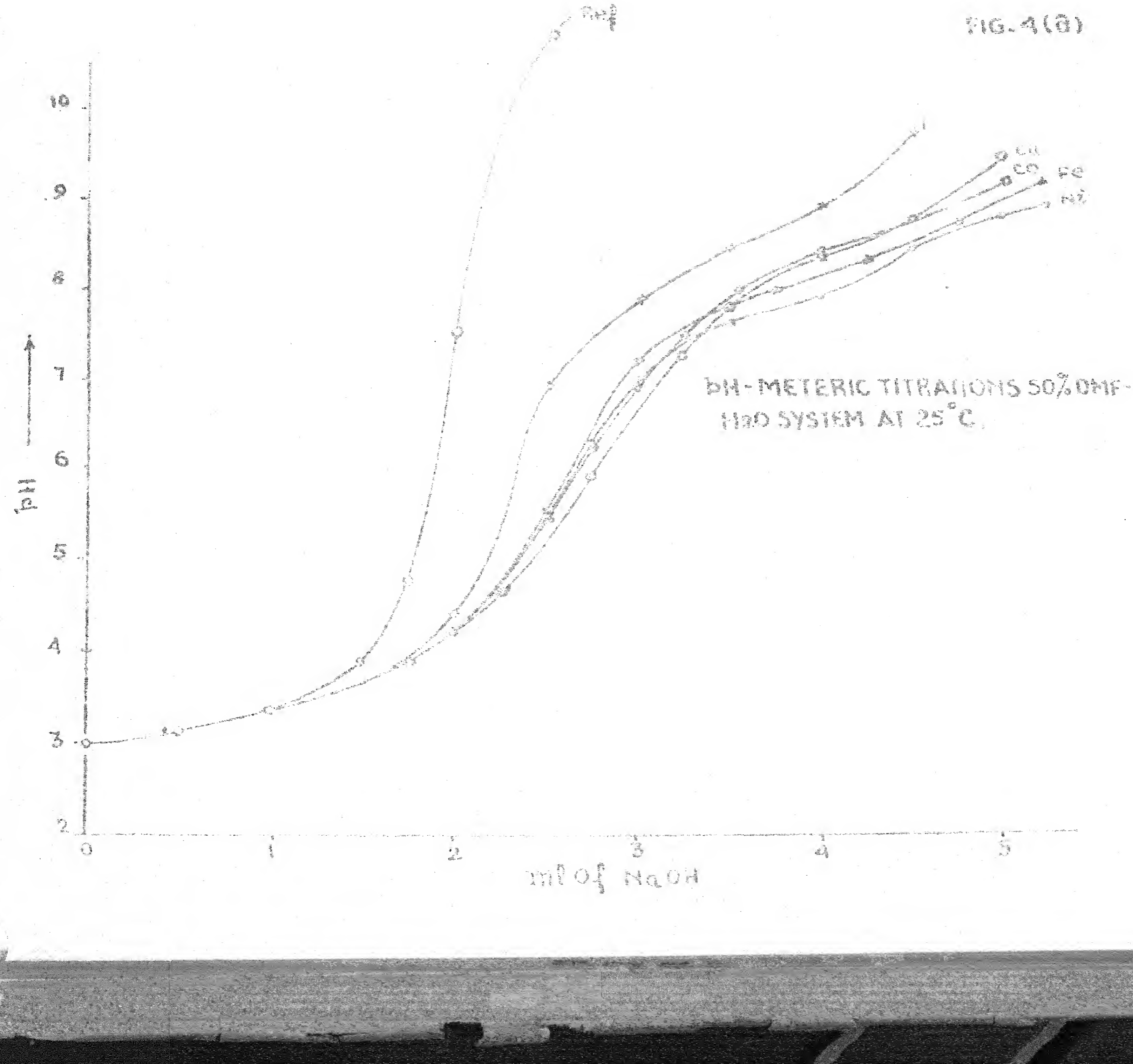
FIG. 3 (C)



pH - METERIC TITRATIONS IN 50% ISO-PROPANOL

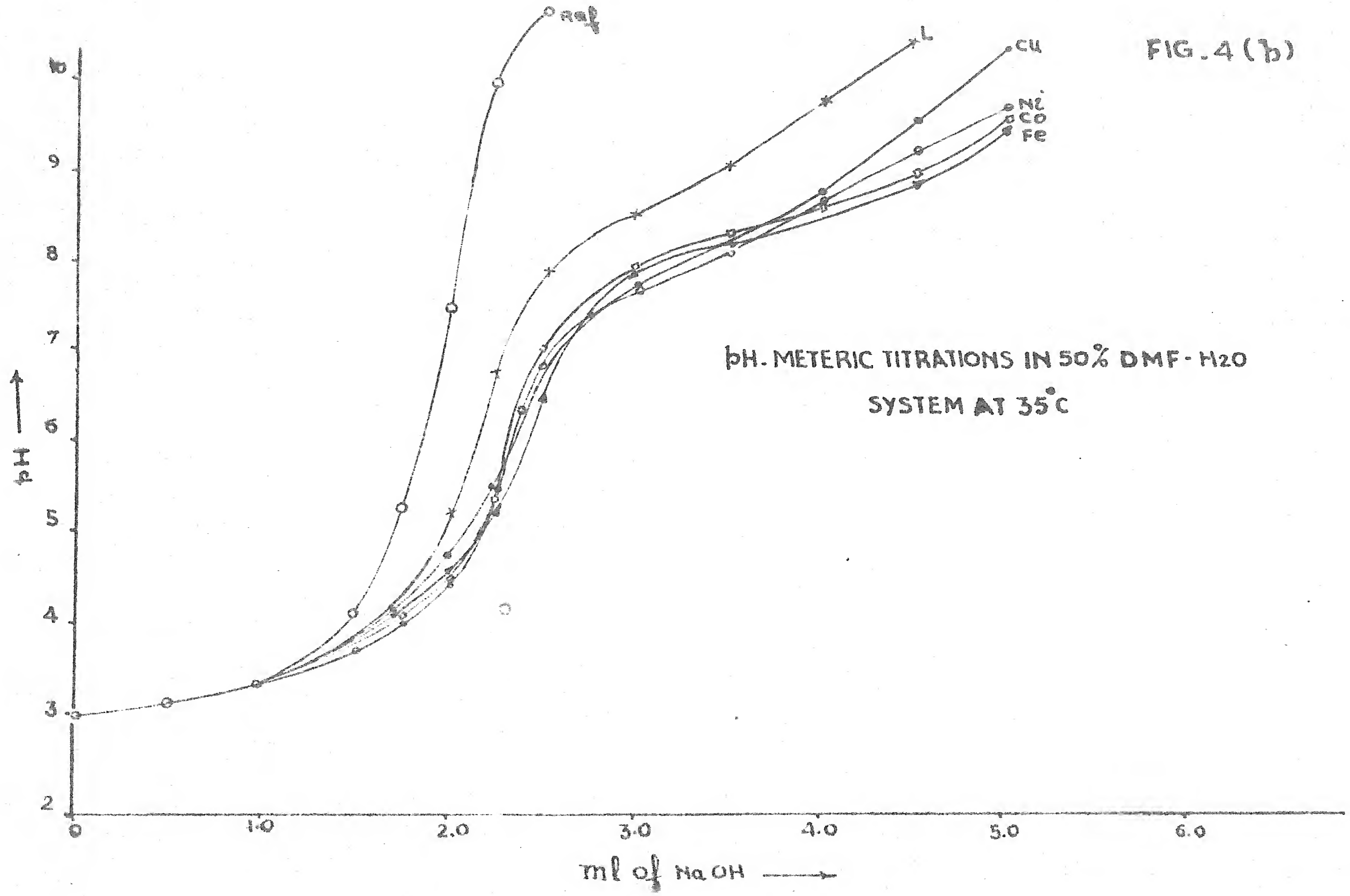
H2O SYSTEM AT 45 °C.

FIG. 4(B)



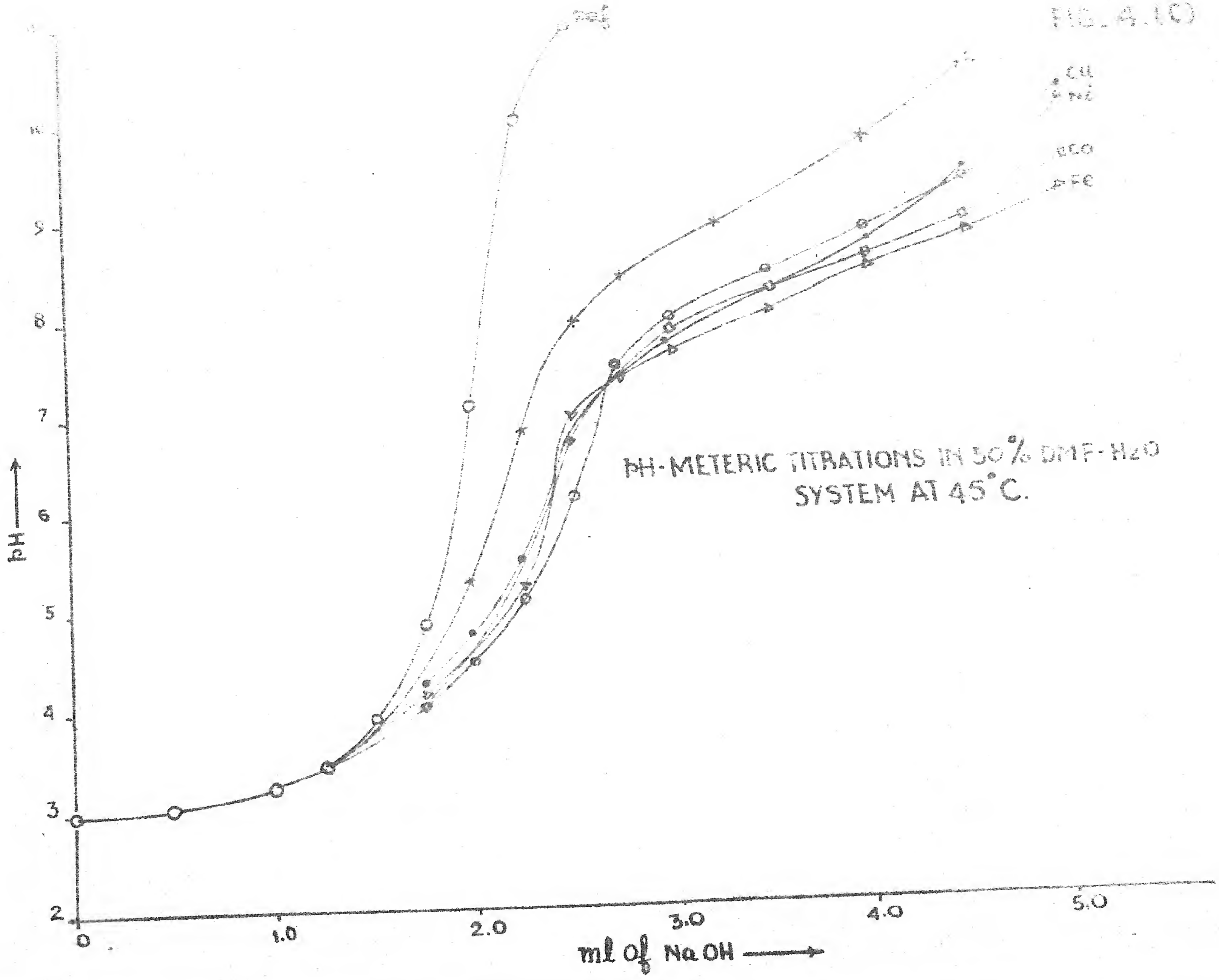
pH
10
9
8
7
6
5
4
3
2
0
1
2
3
4
5
ml of NaOH
Cu
Co
Fe
Ni
pH-METERIC TITRATIONS 50% DMF-H2O SYSTEM AT 25°C.

FIG. 4 (b)



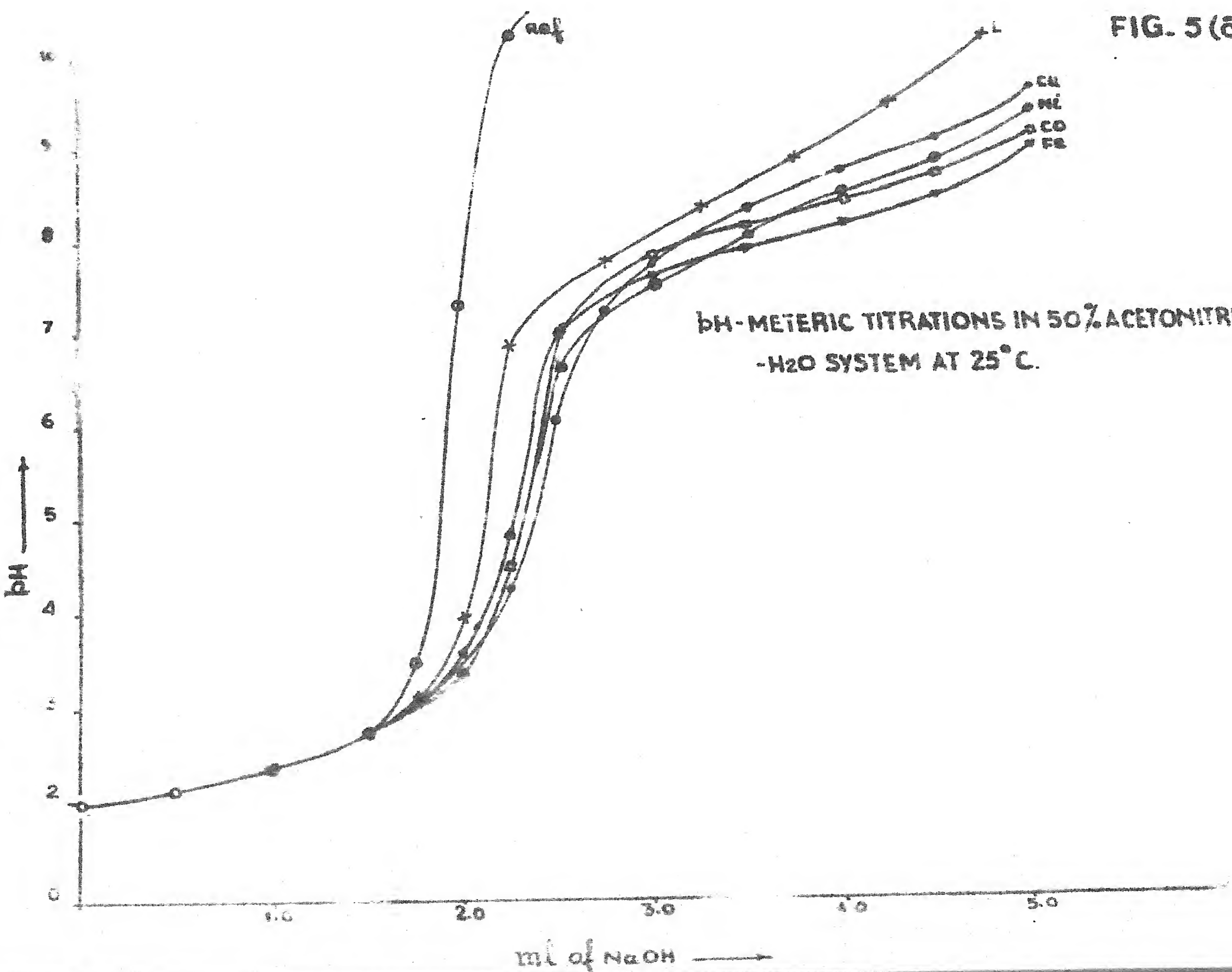
pH. METERIC TITRATIONS IN 50% DMF - H2O SYSTEM AT 35°C

FIG. 4.10



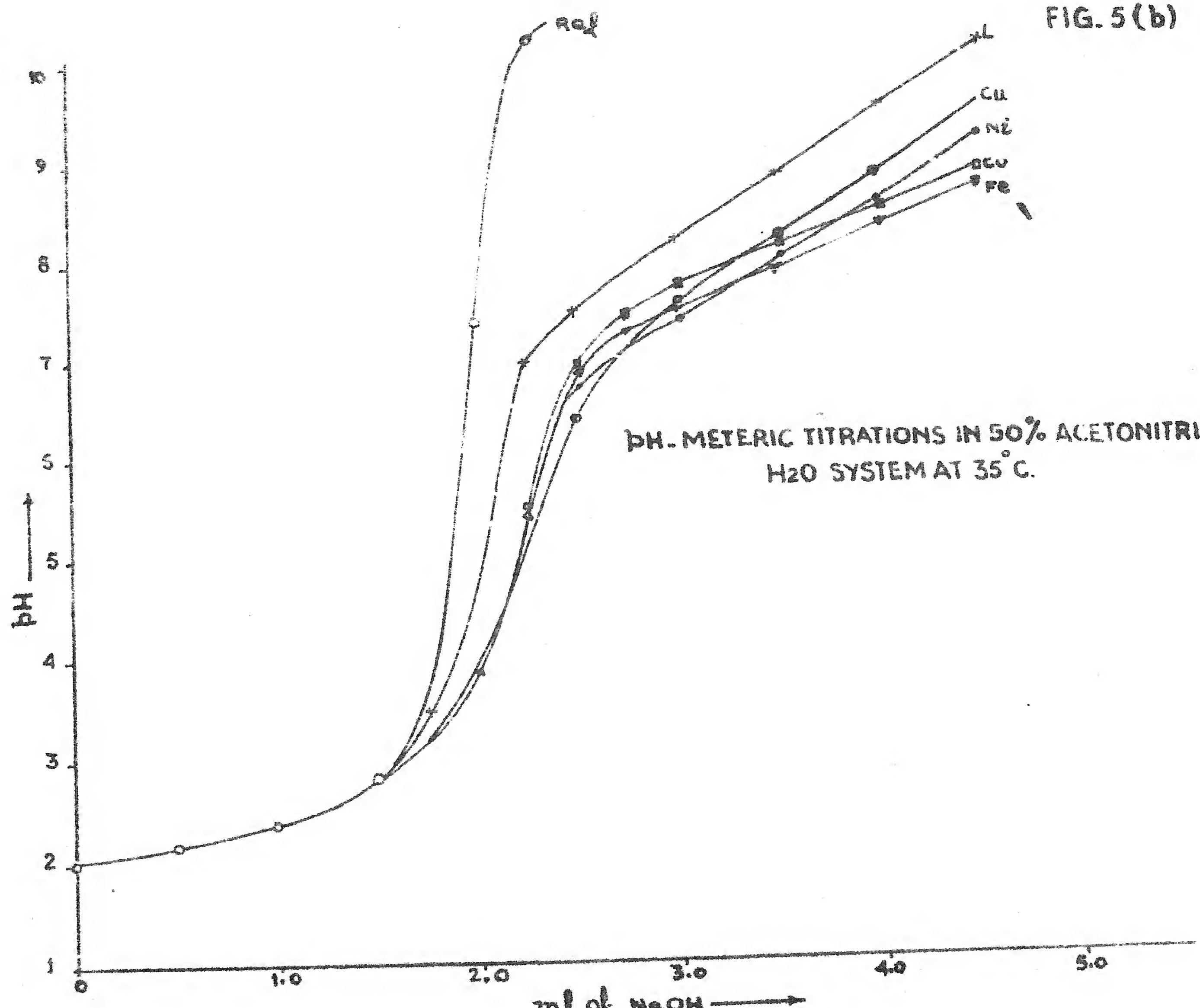
pH-METERIC TITRATIONS IN 50% DMF-H_2O
SYSTEM AT 45°C.

FIG. 5(a)



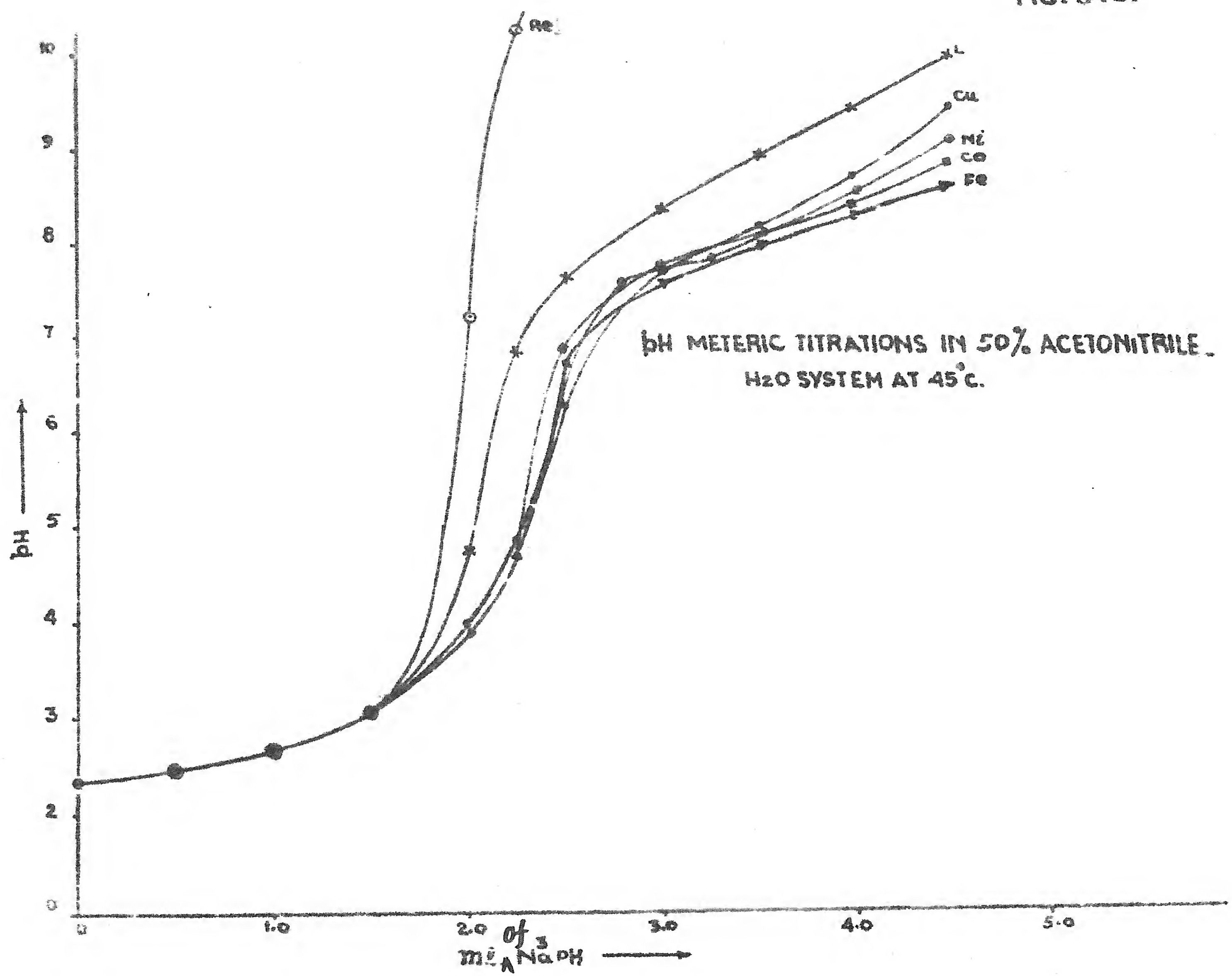
pH-METERIC TITRATIONS IN 50% ACETONITRITE -H2O SYSTEM AT 25°C.

FIG. 5(b)



pH-METERIC TITRATIONS IN 50% ACETONITRILE-H_2O SYSTEM AT 35°C.

FIG. 5(C)



pH METERIC TITRATIONS IN 50% ACETONITRILE - H_2O SYSTEM AT 45°C.

C H A P T E R - V.

Results:

1. Computation of proton-ligand stability constant of ligand at various temperatures and in different mediums.
2. Computation of metal-ligand stability constant at various temperatures and different mediums.
3. Computation of change in free energy (ΔG), change in enthelpy (ΔH) and change in entropy (ΔS) of the complexes.

CHAPTER V

RESULTS:

The calculations from the figures 1 (a,b,c) to 5 (a,b,c) are divided into three sections viz;

(i) determination of proton-ligand stability constant of the ligand,

(ii) determination of metal-ligand stability constant of complex and

(iii) calculation of thermodynamic functions viz; change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) due to complex formation.

(i) Determination of Proton-Ligand Stability Constant of the Ligand:

At any pH, the horizontal distance between the curves from set I and II, measures quite accurately the additional base consumed due to dissociation of H^+ ions from ligand. The number of dissociable H^+ ions can be ascertained by the nature of the curve from set II. If the curve from set II show only one point of inflection, the no. of dissociable H^+ ions will be one and the ligand will have only one proton-ligand stability constant or dissociation constant. On the other hand,

if, the curve from set II show two or more points of inflection, the number of dissociable H^+ ions will be two or more as the case may be, and the ligand will have more than one proton-ligand stability constants or dissociation constnats. In the present investigation the ligand show one point of inflection only, therefore, has only one dissociable H^+ ion. Thus, one proton-ligand stability constant or one dissociation constant is possible in PAP.

The proton-ligand stability constant of the ligand was calculated by Irving-Rossotti Technique[1-5] with necessary corrections as suggested by Uitert and Haas[6] for non-aqueous system. The following equations were used for calculation:

$$\bar{n}_A = Y - \left[\frac{(V'' - V')}{(V^{\circ} + V')} \cdot \frac{N + E^{\circ}}{T_L^{\circ}} \right]$$

$$\text{and } \log pkH = B + \log \frac{\bar{n}_A}{1 - \bar{n}_A}$$

where, $\bar{n}_A \rightarrow$ average no. of ligand-dissociated per H^+ ion.

$V^{\circ} \rightarrow$ initial volume of the solution (50 ml.)

$V' \rightarrow$ volume of alkali added in acid curve (Set I)

$V'' \rightarrow$ volume of alkali added in ligand curve (Set II)

$N \rightarrow$ strength of alkali used for titration (0.2547N)

$E^{\circ} \longrightarrow$ strength of acid in total volume (0.01M)

$T_L^{\circ} \longrightarrow$ conc. of ligand in total volume (0.01M)

$Y \longrightarrow$ no. of dissociable H^+ ions. (for PAP Y = 1)

$B \longrightarrow$ pH - readings.

Thus different $\bar{n}_A$ and logpkH values are obtained for ligand at various temperature as shown in the tables 6 (a,b,c) to 10 (a,b,c). Now $\bar{n}_A$ and logpkH values are plotted (Figs. 6-10). The proton-ligand stability constant of the ligand was read directly from the graph at $\bar{n}_A = 0.5$ (corresponds to the first dissociation). The different values of proton-ligand stability constants and the dissociation constants due to change in temperature and solvents, as read from the graphs, are compiled in the table (26).

(ii) <u>Determination of Metal - Ligand Stability Constants of the Complex:</u>

As in the case of proton-ligand stability constants, the horizontal distance at any pH, between the curve from set II and III, measures quite accurately the additional base consumed or the total amount of the ligand-ions complexed with metals. Hence, a series of $\bar{n}$ values at various pH were obtained alongwith log k i.e. pL.

The $\bar{n}$ and pL values at various pH were calculated for complexes by Irving - Rossotti technique with the following equations :

$$\bar{n} = \frac{(V'' - V')\cdot\left[N + E^{\circ} + T_L^{\circ}\cdot(Y - \bar{n}_A)\right]}{(V^{\circ} + V'')\,\bar{n}_A\,T_M^{\circ}}$$

$$\text{and } pL = \log\left[\frac{1 + pk_1H\cdot\left(\frac{1}{\text{anti log } B}\right) + pk_1H\cdot pk_2H\cdot\left(\frac{1}{\text{anti log } B}\right)^2 + \ldots}{T_L^{\circ} - T_M^{\circ}\cdot\bar{n}} \times \left(\frac{V^{\circ} + V''}{V^{\circ}}\right)\right]$$

Where, $\bar{n}$ ⟶ average no. of ligand bound per metal ion.

V'' ⟶ volume of alkali added with metal curve (Set III)

T_M° ⟶ conc. of metal in total volume. (0.002 M)

pk_1H ⟶ 1st dissociation constant of ligand.

pk_2H ⟶ 2nd dissociation constant of ligand.

The different $\bar{n}$ and logk for complexes with Fe(II), Co(II), Ni(II) and Cu(II) and ligand at different temperature and medium of interaction are given in the tables 11 (a,b,c,d) to 25 (a,b,c,d). The stepwise and overall metal-ligand stability constants of the complexes were obtained from formation curves. The formation curves i.e. plot of $\bar{n}$ against pL, are shown in the figures 11 (a,b,c,d) to 15 (a,b,c,d). The pL values of the

complexes were read directly from the formation curves at $\bar{n} = 0.5$ and $\bar{n} = 1.5$, respectively, for 1:1 and 1:2 complexes. In the present investigation the complexes of Fe(II), Co(II), Ni(II) and Cu(II) with the ligands show the formation of 1:1, and 1:2 complexes. The stability constants for all the complexes in different medium of interaction and at different temperature are given in the table 27.

(iii) <u>Calculation of Thermodynamic Functions of the complexes</u>:

The change in free energy (ΔG), the change in enthalpy (ΔH) and change in entropy (ΔS) of the complexes are calculated by the following equations:

$\Delta G = RT \log_e k$ or $- 2.303\ RT \log k$. and

$$\log \frac{k}{k_1} = \frac{\Delta H}{R} \cdot \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

$$\Delta G = \Delta H - T.\Delta S$$

where, $R \longrightarrow$ molar gas constant (1.987 calories/mole)

$T \longrightarrow$ Temperature.

With the help of table 27 the thermodynamic functions of the complexes were calculated and are reported in the table 28(a,b,c).

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TABLE : 6 (a)

Proton-ligand stability constant at 25°C in 50 % Methanol-H_2O system. of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	log pkH
6.0	1.875	1.975	0.100	0.9489	7.2688
6.5	1.875	2.025	0.150	0.9234	7.5811
7.0	1.875	2.200	0.325	0.8341	7.7014
7.2	1.875	2.250	0.375	0.8086	7.8258
7.5	1.875	2.425	0.550	0.7195	7.9086
7.7	1.875	2.600	0.725	0.6300	7.9311
7.9	1.875	2.750	0.875	0.5534	7.9931
8.0	1.875	2.850	0.975	0.5024	7.9941
8.1	1.875	2.900	1.025	0.4761	8.0598
8.2	1.875	3.025	1.150	0.4131	8.0475

logpkH = 8.015 at $\bar{n}_A$ = 0.5

pkH = 1.023×10^8

TABLE : 6 (b)

Proton-ligand stability constant at 35°C in 50% Methanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.875	2.000	0.125	0.9362	7.1665
6.5	1.875	2.050	0.175	0.9106	7.5079
7.0	1.875	2.175	0.300	0.8469	7.7428
7.4	1.875	2.400	0.525	0.7320	7.8363
7.6	1.875	2.525	0.65	0.6683	7.9042
7.7	1.875	2.600	0.725	0.6300	7.9311
7.8	1.875	2.675	0.80	0.5917	7.9611
7.9	1.875	2.750	0.875	0.5534	7.9931
8.0	1.875	2.875	1.000	0.4897	7.9821
8.1	1.875	2.950	1.075	0.4514	8.0153
8.2	1.875	3.050	1.175	0.4004	8.0246
8.3	1.875	3.125	1.250	0.3621	8.6540

logpkH = 7.98 at $\bar{n}_A$ = 0.5

pkH = 9.550×10^7

TABLE : 6 (e)

Proton-ligand stability constant at 45°C in 50% Methanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.875	1.975	0.100	0.9489	7.2688
6.5	1.875	2.025	0.150	0.9234	7.5811
7.0	1.875	2.125	0.250	0.8725	7.8337
7.2	1.875	2.225	0.350	0.8214	7.8626
7.4	1.875	2.375	0.500	0.7448	7.8651
7.5	1.875	2.475	0.600	0.6938	7.8552
7.6	1.875	2.550	0.675	0.6555	7.8793
7.7	1.875	2.650	0.775	0.6045	7.8842
7.8	1.875	2.750	0.875	0.5534	7.8931
7.9	1.875	2.825	0.950	0.5152	7.9264
8.0	1.875	2.900	1.025	0.4769	7.9598
8.1	1.875	3.000	1.125	0.4258	7.9701
8.2	1.875	3.100	1.225	0.3748	7.9777

logpkH = 7.94 at $\bar{n}_A = 0.5$

pkH = 8.710×10^7

TABLE : 7 (a)

Proton-ligand stability constant at 25°C in 50% Ethanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.875	1.975	0.100	0.9489	7.2688
6.5	1.875	2.000	0.125	0.9362	7.6665
7.0	1.875	2.050	0.125	0.9106	8.0079
7.2	1.875	2.125	0.250	0.8724	8.0348
7.4	1.875	2.250	0.375	0.8086	8.0258
7.6	1.875	2.375	0.500	0.7448	8.0651
7.8	1.875	2.525	0.650	0.6683	8.1042
8.0	1.875	2.700	0.825	0.5789	8.1382
8.2	1.875	2.800	0.925	0.5279	8.2485
8.3	1.875	2.850	0.975	0.5024	8.3041
8.4	1.875	2.950	1.075	0.4514	8.3153
8.5	1.875	3.100	1.225	0.3748	8.2777

logpkH = 8.310 at $\bar{n}_A$ = 0.5

pkH = 2.042×10^8

TABLE : 7 (b)

Proton-ligand stability constant at 35°C in 50% Ethanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	$\log pK^H$
6.0	1.875	1.975	0.100	0.9489	7.2688
6.5	1.875	2.000	0.125	0.9362	7.6665
7.0	1.875	2.075	0.200	0.8979	7.9442
7.2	1.875	2.125	0.250	0.8724	8.0348
7.4	1.875	2.200	0.325	0.8341	8.1014
7.6	1.875	2.300	0.425	0.7831	8.1575
7.8	1.875	2.450	0.575	0.7065	8.1815
8.0	1.875	2.600	0.725	0.6300	8.2311
8.2	1.875	2.775	0.900	0.5407	8.2708
8.3	1.875	2.850	0.975	0.5024	8.3042
8.4	1.875	2.950	1.075	0.4514	8.3153
8.5	1.875	3.050	1.175	0.4003	8.3244
8.6	1.875	3.125	1.250	0.3621	8.3540

$\log pK^H = 8.295$ at $\bar{n}_A = 0.5$

$pK^H = 1.972 \times 10^8$

TABLE : 7 (g)

Proton-ligand stability constant at 45°C in 50% Ethanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{\bar{n}}_A$	logpkH
6.0	1.875	1.975	0.100	0.9489	7.2688
6.5	1.875	2.025	0.150	0.9234	7.5811
7.0	1.875	2.100	0.225	0.8851	7.8866
7.2	1.875	2.175	0.300	0.8469	7.9428
7.4	1.875	2.275	0.400	0.7958	7.9907
7.6	1.875	2.425	0.550	0.7195	8.0086
7.8	1.875	2.600	0.725	0.6300	8.0311
8.0	1.875	2.800	0.925	0.5279	8.0485
8.1	1.875	2.875	1.000	0.4897	8.0821
8.2	1.875	2.975	1.100	0.4386	8.0928
8.3	1.875	3.050	1.175	0.4003	8.1244
8.4	1.875	3.125	1.250	0.3621	8.1540

logpkH = 8.065 at $\bar{\bar{n}}_A$ = 0.5

pkH = 1.161×10^8

TABLE : 8 (a)

proton-ligand stability constant at 25°C in 50% Iso-propanol-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.850	2.125	0.275	0.8596	6.7869
6.5	1.875	2.200	0.325	0.8342	7.2017
7.0	1.875	2.300	0.425	0.7831	7.5575
7.5	1.875	2.450	0.575	0.7066	7.8817
8.0	1.875	2.700	0.825	0.5790	8.1384
8.1	1.900	2.750	0.850	0.5665	8.2162
8.3	1.950	2.900	0.950	0.5159	8.3268
8.4	1.950	2.925	0.975	0.5032	8.4055
8.5	1.950	3.000	1.050	0.4649	8.4405
8.6	1.950	3.075	1.125	0.4207	8.4717

logpkH = 8.39 at $\bar{n}_A$ = 0.5

pkH = 2.455×10^8

TABLE : 8 (b)

Proton-ligand stability constant at 35°C in 50% Iso-propanol-H_2O system of PAP

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.875	2.300	0.425	0.7831	6.5616
6.5	1.875	2.400	0.525	0.7321	6.9366
7.0	1.875	2.525	0.650	0.6683	7.3042
7.5	1.900	2.675	0.775	0.6045	7.6842
8.0	1.900	2.800	0.900	0.5409	8.0712
8.2	1.925	2.875	0.950	0.5157	8.2273
8.4	1.950	2.950	1.000	0.4904	8.3833
8.5	1.975	3.000	1.025	0.4779	8.4616

logpkH = 8.32 at $\bar{n}_A$ = 0.5

pkH = 2.089×10^8

TABLE : 8 (c)

Proton-ligand stability constant at 45°C in 50% Iso-propanol-$-H_2O$ system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.875	2.450	0.575	0.7065	6.3815
6.5	1.875	2.550	0.675	0.6555	6.7794
7.0	1.875	2.650	0.775	0.6045	7.1842
7.5	1.900	2.750	0.850	0.5665	7.6162
7.8	1.900	2.800	0.900	0.5409	7.8712
8.0	1.900	2.850	0.950	0.5155	8.0269
8.2	1.925	2.925	1.000	0.4902	8.1829
8.4	1.950	3.000	1.050	0.4649	8.3389

logpkH = 8.13 at $\bar{n}_A$ = 0.5

pkH = 1.340×10^8

TABLE : 9 (a)

Proton-ligand stability constant at 25°C in 50% DMF $-H_2O$ system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.0	1.90	2.15	0.25	0.8724	6.8348
6.5	1.90	2.20	0.30	0.8469	7.2428
7.0	1.90	2.25	0.35	0.8214	7.6626
7.5	1.90	2.35	0.45	0.7704	8.0257
8.0	1.925	2.575	0.650	0.6686	8.3048
8.2	1.950	2.725	0.775	0.6049	8.3849
8.3	1.950	2.80	0.85	0.5666	8.4164
8.4	1.950	2.925	0.975	0.5029	8.4050
8.5	1.950	2.975	1.025	0.4774	8.4607
8.6	1.950	3.05	1.10	0.4395	8.4943

logpkH = 8.42 at $\bar{n}_A$ = 0.5

pkH= 2.630×10^8

TABLE : 9 (b)

Proton-ligand stability constant at 35°C in 50% DMF $-H_2O$ system of PAP.

pH	C V'	V''	V''-V'	$\bar{n}_A$	logpkH
6.0	1.900	2.400	0.500	0.7449	6.4654
6.5	1.900	2.500	0.600	0.6939	6.8554
7.0	1.900	2.600	0.700	0.6429	7.2553
7.5	1.900	2.700	0.800	0.5919	7.6615
8.0	1.925	2.775	0.850	0.5664	8.1160
8.1	1.925	2.825	0.900	0.5409	8.1712
8.2	1.925	2.850	0.925	0.5284	8.2494
8.3	1.925	2.900	0.975	0.5029	8.3094
8.4	1.950	2.975	1.025	0.4777	8.3612
8.5	1.950	3.025	1.075	0.4522	8.4167

logpkH = 8.30 at $\bar{n}_A = 0.5$

pkH = 2.089×10^8

TABLE : 9 (c)

Proton-ligand stability constant at 45°C in 50% DMF $-H_2O$ system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpKH
6.0	1.900	2.450	0.550	0.7195	6.4090
6.5	1.900	2.575	0.675	0.6557	6.7797
7.0	1.900	2.650	0.750	0.6174	7.2078
7.5	1.900	2.750	0.850	0.5664	7.6160
8.0	1.925	2.825	0.900	0.5412	8.0717
8.1	1.925	2.875	0.950	0.5157	8.1272
8.2	1.925	2.925	1.000	0.4902	8.1829
8.3	1.925	2.950	1.025	0.4774	8.2609
8.4	1.950	3.025	1.075	0.4522	8.3167
8.5	1.950	3.075	1.125	0.4267	8.3717

logpKH = 8.17 at $\bar{n}_A = 0.5$

pKH = 1.479×10^8

TABLE : 10 (a)

Proton-ligand stability constant at 25°C in 50% Acetonitrile-H_2O system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.5	1.900	2.125	0.200	0.898	7.4446
7.0	1.900	2.250	0.350	0.821	7.6615
7.5	1.925	2.375	0.450	0.769	8.0223
7.8	1.925	2.575	0.600	0.668	8.1036
7.9	1.925	2.725	0.800	0.592	8.0616
8.0	1.925	2.925	1.000	0.490	7.9826
8.1	1.950	3.000	1.050	0.465	8.0391
8.2	1.950	3.050	1.100	0.439	8.0935
8.3	1.975	3.125	1.150	0.414	8.1491
8.4	1.975	3.175	1.200	0.389	8.2039

logpkH = 7.99 at $\bar{n}_A$ = 0.5

pkH = 9.772×10^7

TABLE : 10 (b)

Proton-ligand stability constant at 35°C in 50% Acetonitrile-$-H_2O$ system of PAP.

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.5	1.925	2.075	0.150	0.923	7.5787
7.0	1.925	2.225	0.300	0.847	7.7432
7.5	1.950	2.425	0.475	0.758	7.9958
7.8	1.950	2.650	0.700	0.643	8.0555
7.9	1.950	2.950	1.000	0.490	7.8826
8.0	1.975	3.025	1.050	0.465	7.9390
8.1	1.975	3.100	1.125	0.427	7.9723
8.2	1.975	3.150	1.175	0.401	8.0257
8.3	2.000	3.225	1.225	0.376	8.0800

logpkH = 7.89 at $\bar{n}_A = 0.5$

pkH = 7.762×10^7

TABLE : 10 (c)

Proton-ligand stability constant at 45°C in 50% Acetonitrile-H_2O system of PAP

pH	V'	V"	V"-V'	$\bar{n}_A$	logpkH
6.5	1.925	2.175	0.250	0.873	7.3372
7.0	1.925	2.350	0.425	0.783	7.5573
7.5	1.925	2.625	0.700	0.643	7.7000
7.8	1.950	2.925	0.975	0.503	7.8052
7.9	1.950	2.975	1.025	0.478	7.8617
8.0	1.950	3.050	1.100	0.439	7.8935
8.1	1.975	3.150	1.175	0.401	7.9257
8.2	1.975	3.225	1.250	0.363	7.9558
8.3	2.000	3.300	1.300	0.338	8.0080

logpkH = 7.83 at $\bar{n}_A$ = 0.5

pkH = 6.761×10^7

TABLE : 11 (a)

Metal-ligand stability constant at 25°C in 50% Methanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.875	1.925	0.050	0.255	5.9796
4.25	1.900	1.975	0.075	0.382	5.7418
4.50	1.925	2.050	0.125	0.637	5.5171
4.75	1.925	2.100	0.175	0.892	5.2938
5.00	1.950	2.150	0.200	1.019	5.0574
5.25	1.950	2.200	0.250	1.273	4.8375
5.50	1.975	2.250	0.275	1.400	4.6034
5.75	1.975	2.750	0.300	1.528	4.3708
6.00	2.000	2.325	0.325	1.654	4.1243
6.25	2.000	2.425	0.425	2.163	3.9658

$pk_1 = 5.65$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.45}$ at $\bar{n} = 1.5$

$\underline{10.10}$

TABLE : 11 (b)

Metal-ligand stability constant at 25°C in 50% Methanol-$-H_2O$ system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.900	1.95	0.050	0.255	5.7295
4.50	1.925	2.00	0.075	0.382	5.4920
4.75	1.925	2.05	0.125	0.637	5.2672
5.00	1.950	2.10	0.150	0.764	5.0296
5.25	1.950	2.15	0.200	1.019	4.8083
5.50	1.975	2.225	0.250	1.273	4.5885
5.75	1.975	2.30	0.325	1.655	4.3876
6.00	2.000	2.40	0.400	2.036	4.1873

$pk_1 = 5.40$ at $\bar{n} = 0.5$

$pk_2 = 4.45$ at $\bar{n} = 1.5$

9.85

TABLE : 11 (c)

Metal-ligand stability constant at 25°C in 50% Methanol-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.900	1.950	0.050	0.2550	5.7295
4.50	1.925	2.000	0.075	0.3823	5.4920
4.75	1.925	2.025	0.100	0.5097	5.2543
5.00	1.950	2.075	0.125	0.6369	5.0172
5.25	1.950	2.125	0.175	0.8916	4.7947
5.50	1.975	2.200	0.225	1.145	4.5732
5.75	1.975	2.250	0.275	1.400	4.3546
6.00	2.000	2.350	0.350	1.781	4.1510
6.25	2.000	2.400	0.400	2.036	3.9469

$pk_1 = 5.30$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.30}$ at $\bar{n} = 1.5$

$\underline{9.60}$

TABLE : 11 (d)

Metal-ligand stability constant at 25°C in 50% Methanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.900	1.925	0.025	0.127	5.7180
4.50	1.925	1.975	0.050	0.254	5.4797
4.75	1.925	2.000	0.075	0.382	5.2422
5.25	1.950	2.125	0.175	0.891	4.7942
5.50	1.975	2.175	0.200	1.018	4.5592
5.75	1.975	2.225	0.250	1.273	4.3398
6.00	2.00	2.300	0.300	1.527	4.1175
6.25	2.000	2.375	0.375	1.908	3.9394

$pk_1 = 5.05$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.15}$ at $\bar{n} = 1.5$

$\underline{9.20}$

TABLE : 12 (a)

Metal-ligand stability constant at 35°C in 50% Methanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.50	1.950	1.925	0.025	0.127	5.5082
4.75	1.975	2.025	0.050	0.254	5.2980
5.00	1.975	2.050	0.075	0.382	5.0316
5.25	2.000	2.100	0.100	0.509	4.7944
5.50	2.000	2.150	0.150	0.763	4.5706
5.75	2.000	2.175	0.175	0.890	4.3347
6.00	2.000	2.225	0.225	1.145	4.1145
6.25	2.000	2.275	0.275	1.339	3.8978
6.50	2.050	2.375	0.325	1.652	3.6862

$pk_1 = 5.80$ at $\bar{n} = 0.5$

$pk_2 = 3.80$ at $\bar{n} = 1.5$

$\overline{9.60}$

TABLE : 12 (b)

Metal-ligand stability constant at 35°C in 50% Methanol-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.925	2.000	0.075	0.332	6.0312
4.25	1.950	2.050	0.100	0.509	5.7934
4.75	1.975	2.100	0.125	0.636	5.3065
5.00	2.000	2.150	0.150	0.763	5.0696
5.25	2.000	2.175	0.175	0.890	4.8330
5.50	2.000	2.200	0.200	1.018	4.5975
5.75	2.000	2.225	0.225	1.145	4.3625
6.00	2.000	2.250	0.250	1.273	4.1294
6.50	2.050	2.325	0.275	1.398	3.6543
7.00	2.150	2.550	0.400	2.030	3.2677

$pk_1 = 5.85$ at $\bar{n} = 0.5$

$pk_2 = \underline{3.55}$ at $\bar{n} = 1.5$

$\underline{9.40}$

TABLE : 12 (e)

Metal-ligand stability constant at 35°C in 50% Methanol-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.5	1.050	1.975	0.025	0.127	5.5082
4.75	1.975	2.025	0.050	0.254	5.2698
5.00	1.975	2.050	0.075	0.381	5.0316
5.25	2.000	2.100	0.100	0.509	4.7944
5.50	2.000	2.125	0.125	0.636	4.5519
5.75	2.000	2.200	0.200	1.018	4.3481
6.00	2.000	2.275	0.275	1.399	4.1442
6.25	2.000	2.350	0.350	1.782	3.9462

$pk_1 = 4.85$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.10}$ at $\bar{n} = 1.5$

$\underline{8.95}$

TABLE : 12 (d)

Metal-ligand stability constant at 35°C in 50% Methanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.5	1.050	1.975	0.025	0.127	5.5082
4.75	1.975	2.025	0.050	0.254	5.2698
5.00	1.975	2.050	0.075	0.381	5.0316
5.25	2.000	2.100	1.100	1.509	4.7944
5.50	2.000	2.125	0.125	0.636	4.5519
5.75	2.000	2.200	0.200	1.018	4.3481
6.00	2.000	2.275	0.275	1.399	4.1442
6.25	2.000	2.350	0.350	1.782	3.9462

$pk_1 = 4.85$ at $\bar{n} = 0.5$

$pk_2 = 4.10$ at $\bar{n} = 1.5$

$\underline{8.95}$

TABLE : 13 (a)

Metal-ligand stability constant at 45°C in 50% Methanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.900	1.950	0.050	0.255	5.7998
4.50	1.925	2.000	0.075	0.382	5.5612
4.75	1.925	2.075	0.100	0.509	5.3232
5.00	1.950	2.150	0.200	1.019	5.1260
5.25	1.975	2.200	0.225	1.145	4.8904
5.50	1.975	2.225	0.250	1.273	4.6598
5.75	2.000	2.275	0.275	1.400	4.4219
6.00	2.000	2.300	0.300	1.527	4.1910
6.25	2.000	2.325	0.325	1.654	3.9590

$pk_1 = 5.30$ at $\bar{n} = 0.5$

$pk_2 = 4.25$ at $\bar{n} = 1.5$

9.55

TABLE : 13 (b)

Metal-ligand stability constant at 45°C in 50% Methanol-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.50	1.925	1.975	0.050	0.255	5.5491
4.75	1.925	2.000	0.075	0.282	5.3113
5.00	1.950	2.050	0.100	0.509	5.0736
5.25	1.975	2.125	0.150	0.764	4.8496
5.50	1.975	2.150	0.175	0.892	4.6137
5.75	2.000	2.200	0.200	1.019	4.3784
6.00	2.000	2.275	0.275	1.400	4.1738
6.25	2.000	2.375	0.375	1.903	3.9934

$pk_1 = 5.10$ at $\bar{n} = 0.5$

$pk_2 = 4.10$ at $\bar{n} = 1.5$

9.20

TABLE : 13 (c)

Metal-ligand stability constant at 45°C in 50% Methanol - H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{\bar{n}}$	pL
4.75	1.925	1.975	0.050	0.255	5.2992
5.00	1.950	2.025	0.075	0.382	5.0617
5.25	1.975	2.075	0.100	0.509	4.8242
5.50	1.975	2.100	0.125	0.637	4.5875
5.75	2.000	2.150	0.150	0.764	4.3514
6.00	2.000	2.175	0.175	0.892	4.1167
6.25	2.000	2.000	0.200	1.019	3.8835
6.50	2.025	2.250	0.225	1.145	3.6533
6.75	2.075	2.375	0.300	1.527	3.4606

$pk_1 = 4.85$ at $\bar{\bar{n}} = 0.5$

$pk_2 = \underline{3.50}$ at $\bar{\bar{n}} = 1.5$

$\underline{8.35}$

TABLE : 13 (d)

Metal-ligand stability constant at 45°C in 50% Methanol-$-H_2O$ system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.75	1.925	1.950	0.025	0.127	5.2879
5.00	1.950	2.005	0.050	0.255	5.0496
5.25	1.975	2.050	0.075	0.384	4.8125
5.50	1.975	2.075	0.100	0.509	4.5777
5.75	2.000	2.125	0.125	0.637	4.3388
6.00	2.000	2.150	0.150	0.764	4.1032
6.25	2.000	2.200	0.200	1.019	3.8835
6.50	2.025	2.250	0.250	1.275	3.6682
6.75	2.075	2.400	0.325	1.654	3.4751

$pk_1 = 4.60$ at $\bar{n} = 0.5$

$pk_2 = \underline{3.55}$ at $\bar{n} = 1.5$

$\underline{8.15}$

TABLE : 14 (a)

Metal-ligand stability constant at 25°C in 50% Ethanol-$-H_2O$ system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.0	1.75	1.825	0.075	0.2908	7.3609
3.5	1.725	1.90	0.125	0.6511	6.8868
4.0	1.875	2.05	0.175	0.9098	6.4147
4.5	1.900	2.100	0.200	1.0393	5.9292
5.0	1.95	2.175	0.225	1.1680	5.4433
5.5	1.975	2.225	0.25	1.2972	4.9601
6.0	1.975	2.250	0.275	1.4269	4.4772
6.5	2.00	2.300	0.30	1.5559	3.9981
7.0	2.05	2.375	0.325	1.6840	3.5293

$pk_1 = 7.15$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.15}$ at $\bar{n} = 1.5$

$\underline{11.30}$

TABLE : 14 (b)

Metal-ligand stability constant at 25°C in 50% Ethanol-$-H_2O$ system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.5	1.775	1.850	0.075	0.3907	6.8612
4.0	1.875	2.00	0.125	0.6498	6.3875
4.5	1.900	2.075	0.175	0.9094	5.9150
5.0	1.95	2.15	0.200	1.0383	5.4296
5.5	1.975	2.20	0.225	1.1675	4.9449
5.75	1.975	2.225	0.250	1.2972	4.7106
6.0	1.975	2.250	0.275	1.4269	4.4772
6.25	1.975	2.275	0.300	1.5567	4.2452
6.50	2.000	2.375	0.375	1.9449	4.0500
6.75	2.025	2.475	0.450	2.3328	3.8658

$pk_1 = 6.650$ at $\bar{n} = 0.5$

$pk_2 = 4.30$ at $\bar{n} = 1.5$

$\overline{10.95}$

TABLE : 14 (c)

Metal-ligand stability constant at 25°C in 50% Ethanol-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.25	1.700	1.775	0.075	0.3912	7.1106
3.5	1.750	1.900	0.150	0.7817	6.9001
4.00	1.875	2.075	0.200	1.0398	6.4289
5.0	1.950	2.175	0.225	1.1675	5.4442
5.5	1.975	2.225	0.250	1.2972	4.9601
6.5	2.000	2.275	0.275	1.4262	3.9819
7.0	2.050	2.350	0.300	1.5544	3.5124

$pk_1 = 7.05$ at $\bar{n} = 0.5$

$pk_2 = 3.65$ at $\bar{n} = 1.5$

$\overline{10.70}$

TABLE : 14 (d)

Metal-ligand stability constant at 25°C in 50% Ethanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.5	1.90	1.975	0.075	0.3897	5.8622
4.75	1.925	2.025	0.100	0.5194	5.6250
5.00	1.950	2.075	0.125	0.6489	5.3882
5.5	1.975	2.125	0.150	0.7783	4.9025
5.75	1.975	2.20	0.225	1.1675	4.6954
6.00	1.975	2.30	0.325	1.6864	4.5103
6.25	1.975	2.375	0.400	2.0756	4.3169
6.50	2.000	2.45	0.450	2.3339	4.1106

$pk_1 = 5.65$ at $\bar{n} = 0.5$

$pk_2 = 4.55$ at $\bar{n} = 1.5$

$\underline{10.20}$

TABLE : 15 (a)

Metal-ligand stability constant at 35°C in 50% Ethanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.5	1.850	1.875	0.025	0.1300	6.8223
4.0	1.900	2.000	0.100	0.5196	6.3596
4.25	1.900	2.050	0.150	0.7794	6.1360
4.5	1.925	2.100	0.175	0.9089	5.9000
5.0	1.95	2.15	0.200	1.0383	5.4144
6.00	2.000	2.225	0.225	1.1669	4.4314
6.25	2.000	2.250	0.250	1.2966	4.1983
6.5	2.025	2.375	0.350	1.8144	4.0177

$pk_1 = 6.35$ at $\bar{n} = 0.5$

$pk_2 = 4.15$ at $\bar{n} = 1.5$

$\underline{10.50}$

TABLE : 15 (b)

Metal-ligand stability constant at 35°C in 50% Ethanol-H_2O system with Ni(II).

pH	V''	V'''	V'''-V''	$\bar{n}$	pL
4.0	1.900	1.975	0.075	0.3897	6.3469
4.25	1.900	2.000	0.100	0.5196	6.1097
4.5	1.925	2.095	0.150	0.7791	6.8862
4.75	1.925	2.100	0.175	0.9089	5.6500
5.00	1.950	2.150	0.200	1.0383	5.4144
5.50	1.975	2.200	0.225	1.1675	4.9298
6.00	2.000	2.500	0.250	1.2966	4.4486
6.50	2.025	2.300	0.275	1.4256	3.9671
7.00	2.050	2.400	0.350	1.8135	3.5324

$pk_1 = 6.125$ at $\bar{n} = 0.5$

$pk_2 = 3.875$ at $\bar{n} = 1.5$

$\overline{10.000}$

TABLE : 15 (e)

Metal-ligand stability constant at 35°C in 50% Ethanol-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.5	1.925	1.975	0.050	0.2597	5.8350
5.0	1.950	2.025	0.075	0.3893	5.3475
5.25	1.950	2.075	0.125	0.6489	5.1235
5.5	1.975	2.125	0.150	0.7783	4.8871
5.75	1.975	2.225	0.250	1.2972	4.6955
6.00	2.000	2.300	0.300	1.5559	4.4785
6.25	2.000	2.350	0.350	1.8152	4.2647

$pk_1 = 5.25$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.50}$ at $\bar{n} = 1.5$

$\underline{9.75}$

TABLE : 15 (d)

Metal-ligand stability constant at 35°C in 50% Ethanol-$-H_2O$ system with Fe(II).

B	V"	V"'	V"'-V"	$\bar{n}$	pL
4.0	1.900	1.950	0.050	0.2598	6.3347
4.25	1.900	1.975	0.075	0.3897	6.0970
4.50	1.925	2.025	0.100	0.5194	5.8598
4.75	1.925	2.050	0.125	0.6492	5.6229
5.0	1.950	2.100	0.150	0.7787	5.3865
5.50	1.975	2.150	0.175	0.9080	4.9009
6.00	2.000	2.200	0.200	1.0373	4.4167
6.5	2.025	2.250	0.225	1.1664	3.9363
7.0	2.050	2.375	0.325	1.6840	3.5148
7.5	2.25	2.625	0.375	1.9356	3.0943

$pk_1 = 5.875$ at $\bar{n} = 0.5$

$pk_2 = 3.65$ at $\bar{n} = 1.5$

$\underline{\overline{9.525}}$

TABLE : 16 (a)

Metal-ligand stability constant at 45°C in 50% Ethanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.5	1.825	1.875	0.050	0.2602	6.6040
4.0	1.950	2.050	0.100	0.5191	6.1299
4.5	1.975	2.100	0.125	0.6486	5.6431
5.0	1.975	2.125	0.150	0.7783	5.1567
5.25	1.975	2.150	0.175	0.9080	4.9200
5.50	2.000	2.200	0.200	0.0373	4.6857
6.00	2.000	2.225	0.225	1.1669	4.2028
6.25	2.025	2.275	0.250	1.2960	3.9711
6.50	2.025	2.325	0.300	1.5552	3.7580
7.00	2.100	2.450	0.350	1.8118	3.3169

$pk_1 = 6.15$ at $\bar{n} = 0.5$

$pk_2 = \underline{3.80}$ at $\bar{n} = 1.5$

$\underline{9.95}$

TABLE : 16 (b)

Metal-ligand stability constant in 50% Ethanol- H_2O system at 45°C with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.5	1.800	1.825	0.025	0.1301	6.5919
4.0	1.950	2.025	0.075	0.3893	6.1173
4.5	1.975	2.075	0.100	0.5189	5.6302
5.0	1.975	2.100	0.125	0.6486	5.1434
5.25	1.975	2.125	0.150	0.7783	4.9071
5.50	2.000	2.175	0.175	0.9076	4.6715
5.75	2.000	2.200	0.200	1.0373	4.4366
6.00	2.000	2.275	0.275	1.4262	4.2337
6.25	2.025	2.400	0.375	1.9440	4.0556

$pk_1 = 5.70$ at $\bar{n} = 0.5$

$pk_2 = 4.20$ at $\bar{n} = 1.5$

$\overline{9.90}$

TABLE : 16 (c)

Metal-ligand stability constant at 45°C in 50% Ethanol-$-H_2O$ system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.5	1.975	2.000	0.025	0.1297	5.5934
5.0	1.975	2.075	0.100	0.5189	5.1304
5.25	1.975	2.100	0.125	0.6486	4.8937
5.50	2.000	2.150	0.150	0.7779	4.6577
5.75	2.000	2.250	0.250	1.2966	4.4665
6.00	2.000	2.300	0.300	1.5559	4.2499
6.25	2.025	2.475	0.400	2.0736	4.0751

$pk_1 = 5.15$ at $\bar{n} = 0.5$

$pk_2 = 4.30$ at $\bar{n} = 1.5$

9.45

TABLE : 16 (d)

Metal-ligand stability constant at 45°C in 50% Ethanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.0	1.950	2.000	0.050	0.2595	6.1050
4.5	1.975	2.050	0.075	0.3891	5.6176
5.0	1.975	2.100	0.125	0.6486	5.1434
5.25	1.975	2.125	0.150	0.7783	4.9071
5.50	2.000	2.175	0.175	0.9076	4.6753
6.00	2.000	2.200	0.200	1.0373	4.1882
6.25	2.025	2.250	0.225	1.1664	3.9560
6.50	2.025	2.275	0.250	1.2960	3.7261
6.75	2.050	2.325	0.275	1.4249	3.5005
7.00	2.100	2.400	0.300	1.5529	3.2825
7.25	2.150	2.475	0.325	1.6807	3.0756

$pk_1 = 5.40$ at $\bar{n} = 0.5$

$pk_2 = 3.35$ at $\bar{n} = 1.5$

$\overline{8.75}$

TABLE : 17 (a)

Metal-ligand Stability constant at 25°C in 50% Iso-propanol-H_2O system with Cu(II).

pH	V''	V'''	V'''-V''	$\bar{n}$	pL
3.75	1.75	1.825	0.075	0.383	6.690
4.00	1.85	2.000	0.150	0.765	6.479
4.25	1.90	2.100	0.200	1.020	6.257
4.50	1.925	2.200	0.275	1.402	6.052
5.00	2.05	2.375	0.325	1.653	5.534
5.50	2.15	2.500	0.350	1.776	5.103
6.25	2.35	2.725	0.275	1.896	4.374

$pk_1 = 6.60$ at $\bar{n} = 0.5$

$pk_2 = 5.80$ at $\bar{n} = 1.5$

$\underline{12.40}$

TABLE : 17 (b)

Metal-ligand stability constant at 25°C in 50% Iso-propanol-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.925	0.075	0.382	6.441
4.25	1.10	2.025	0.125	0.637	6.217
4.50	1.925	2.125	0.200	1.019	6.007
4.75	2.00	2.225	0.225	1.145	5.772
5.00	2.05	2.300	0.25	1.271	5.537
5.50	2.15	2.475	0.325	1.649	5.035
6.00	2.275	2.625	0.350	1.772	4.604
6.50	2.35	2.775	0.425	2.148	4.163

$pk_1 = 6.30$ at $\bar{n} = 0.5$

$pk_2 = \underline{5.25}$ at $\bar{n} = 1.5$

$\underline{11.55}$

TABLE : 17 (e)

Metal-ligand stability constant at 25°C in 50% Iso-propanol-$-H_2O$ system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.900	0.050	0.255	6.429
4.25	1.90	2.000	0.100	0.510	6.204
4.50	1.925	2.100	0.175	0.892	5.994
4.75	2.00	2.200	0.200	1.018	5.758
5.00	2.05	2.275	0.225	1.142	5.522
5.50	2.15	2.400	0.250	1.268	5.038
5.75	2.25	2.550	0.300	1.519	4.820
6.00	2.275	2.600	0.325	1.645	4.587
6.50	2.35	2.750	0.400	2.007	3.932

$pk_1 = 6.20$ at $\bar{n} = 0.5$

$pk_2 = 4.85$ at $\bar{n} = 1.5$

$\underline{11.0}$

TABLE : 17 (d)

Metal-ligand stability constant at 25°C in 50% Iso-propanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.900	0.050	0.255	6.4294
4.25	1.90	2.000	0.100	1.510	6.2039
4.50	1.925	2.125	0.200	1.019	6.0073
5.00	2.05	2.275	0.225	1.144	5.5224
5.50	2.15	2.400	0.250	1.268	5.0382
5.75	2.225	2.500	0.275	1.394	4.8043
6.00	2.275	2.575	0.300	1.519	4.5710
6.50	2.35	2.750	0.400	2.022	4.1436

$pk_1 = 6.25$ at $\bar{n} = 0.5$

$pk_2 = 4.65$ at $\bar{n} = 1.5$

$\underline{10.90}$

TABLE : 18(a)

Metal-ligand stability constant at 35°C in 50% Iso-propanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.75	1.80	1.85	0.05	0.255	6.608
4.00	1.85	1.975	0.125	0.637	6.396
4.25	1.90	2.10	0.20	1.019	6.187
4.50	1.95	2.175	0.225	1.144	5.951
4.75	2.00	2.25	0.25	1.268	5.716
5.00	2.025	2.325	0.30	1.519	5.497
5.50	2.125	2.475	0.325	1.645	5.015
5.75	2.20	2.625	0.375	1.896	4.800

$pk_1 = 6.50$ at $\bar{n} = 0.5$

$pk_2 = 5.50$ at $\bar{n} = 1.5$

12.00

TABLE : 18 (b)

Metal-ligand stability constant at 35°C in 50% Iso-propanol-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.90	0.05	0.255	6.355
4.25	1.90	2.00	0.10	0.510	6.134
4.50	1.95	2.10	0.15	0.705	5.910
4.75	2.00	2.20	0.20	1.019	5.688
5.00	2.025	2.25	0.225	1.144	5.452
5.25	2.10	2.375	0.275	1.394	5.232
5.50	2.15	2.450	0.300	1.519	4.998
5.75	2.20	2.55	0.35	1.776	4.784
6.00	2.275	2.650	0.375	1.896	4.552

$pk_1 = 6.15$ at $\bar{n} = 0.5$

$pk_2 = 5.05$ at $\bar{n} = 1.5$

11.20

TABLE : 18 (c)

Metal-ligand stability constant at 35°C in 50% Iso-propanol-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.90	1.975	0.075	0.3824	6.122
4.50	1.95	2.075	0.125	0.6375	5.897
5.00	2.025	2.25	0.225	1.144	5.452
5.25	2.10	2.35	0.250	1.268	5.217
5.50	2.15	2.425	0.275	1.394	5.983
6.00	2.275	2.600	0.325	1.645	4.517

$pk_1 = 6.00$ at $\bar{n} = 0.5$

$pk_2 = 4.80$ at $\bar{n} = 1.5$

$\underline{10.80}$

TABLE : 18 (d)

Metal-ligand stability constant at 35°C in 50% Iso-propanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.90	1.95	0.05	0.255	6.169
4.50	1.95	2.05	0.10	0.510	5.884
5.00	2.025	2.175	0.125	0.6375	5.398
5.25	2.10	2.275	0.175	0.8921	5.175
5.50	2.15	2.400	0.25	1.268	4.968
5.75	2.20	2.475	0.275	1.394	4.734
6.00	2.275	2.600	0.325	1.645	4.517
6.25	2.35	2.70	0.35	1.776	4.287

pk_1 = 5.90 at $\bar{n}$ = 0.5

pk_2 = 4.65 at $\bar{n}$ = 1.5

10.55

TABLE 19(a)

Metal-ligand stability constant at 45°C in 50% Iso-propanol-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.75	1.80	1.85	0.050	0.255	6.418
4.00	1.85	1.95	0.100	0.510	6.193
4.25	1.90	2.05	0.150	0.765	5.969
4.50	1.95	2.125	0.175	0.891	5.733
4.75	2.00	2.200	0.200	1.017	5.498
5.00	2.05	2.325	0.275	1.397	5.292
5.25	2.10	2.40	0.30	1.523	5.059
5.50	2.15	2.475	0.325	1.648	4.826
6.00	2.25	2.600	0.35	1.775	4.345

$pk_1 = 6.20$ at $\bar{n} = 0.5$

$pk_2 = 5.10$ at $\bar{n} = 1.5$

$\underline{\quad 11.30 \quad}$

TABLE : 19 (b)

Metal-ligand stability constant at 45°C in 50% Iso-propanol $-H_2O$ system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.925	0.075	0.382	6.181
4.25	1.90	2.00	0.100	0.510	5.944
4.50	1.95	2.025	0.125	0.637	5.706
4.75	2.00	2.175	0.175	0.891	5.484
5.00	2.05	2.25	0.200	1.017	5.248
5.25	2.10	2.35	0.25	1.270	5.027
5.50	2.15	2.45	0.30	1.523	4.809
5.75	2.20	2.55	0.35	1.775	4.597
6.00	2.25	2.625	0.375	1.899	4.363

$pk_1 = 5.95$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.85}$ at $\bar{n} = 1.5$

$\underline{10.80}$

TABLE : 19 (c)

Metal-ligand stability constant at 45 °C in 50% Iso-propanol - H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.90	1.975	0.075	0.383	5.931
4.50	1.95	2.05	0.10	0.510	5.694
4.75	2.00	2.15	0.15	0.765	5.470
5.00	2.05	2.225	0.175	0.891	5.254
5.25	2.10	2.325	0.225	1.143	5.013
5.50	2.15	2.425	0.275	1.397	4.793
5.75	2.20	2.525	0.325	1.648	4.577
6.00	2.25	2.625	0.375	1.899	4.363

$pk_1 = 4.70$ at $\bar{n} = 0.5$

$pk_2 = \underline{5.70}$ at $\bar{n} = 1.5$

$\underline{10.40}$

TABLE : 19 (d)

Metal-ligand stability constant at 45°C in 50% Iso-propanol-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.90	1.95	0.05	0.255	5.919
4.50	1.95	2.05	0.10	0.510	5.694
4.75	2.00	2.125	0.125	0.637	5.457
5.00	2.05	2.20	0.15	0.765	5.221
5.25	2.10	2.30	0.20	1.017	4.999
5.50	2.15	2.40	0.25	1.270	4.777
5.75	2.20	2.50	0.30	1.525	4.561
6.00	2.25	2.60	0.35	1.775	4.345
6.25	2.30	2.70	0.40	2.025	4.134

$pk_1 = 5.70$ at $\bar{n} = 0.5$

$pk_2 = 4.60$ at $\bar{n} = 1.5$

$\overline{\underline{10.30}}$

TABLE : 20 (a)

Metal-ligand stability constant at 25°C in 50% DMF $-H_2O$ system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.75	1.80	1.85	0.05	0.260	6.7089
4.00	1.85	1.975	0.125	0.649	6.4972
4.25	1.925	2.100	0.175	0.908	6.2752
4.50	1.950	2.175	0.225	1.167	6.0543
4.75	1.975	2.225	0.250	1.296	5.8194
5.00	2.00	2.275	0.275	1.425	5.5857
5.25	2.025	2.35	0.325	1.682	5.3680
5.50	2.05	2.425	0.375	1.939	5.1543
5.75	2.10	2.55	0.400	2.068	4.9246

$pk_1 = 6.58$ at $\bar{n} = 0.5$

$pk_2 = 5.52$ at $\bar{n} = 1.5$

12.10

TABLE : 20 (b)

Metal-ligand stability constant at 25°C in 50% DMF $-H_2O$ system with Ni (II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.925	0.075	0.390	6.4716
4.25	1.925	2.05	0.125	0.649	6.2479
4.50	1.950	2.25	0.175	0.908	6.0254
4.75	1.975	2.20	0.225	1.167	5.8045
5.00	2.000	2.278	0.275	1.425	5.5851
5.25	2.025	2.325	0.300	1.554	5.3818
5.50	2.05	2.375	0.325	1.682	5.1185
5.75	2.10	2.450	0.350	1.812	4.8875
6.00	2.15	2.550	0.400	2.068	4.6753

$pk_1 = 6.38$ at $\bar{n} = 0.5$

$pk_2 = 5.44$ at $\bar{n} = 1.5$

$\underline{\overline{11.82}}$

TABLE : 20 (c)

Metal-ligand stability constant at 25°C in 50% DMF -H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.850	1.90	0.05	0.26	6.4594
4.25	1.925	2.025	0.10	0.519	6.2349
4.50	1.950	2.10	0.15	0.778	6.0116
4.75	1.975	2.175	0.20	1.038	5.7898
5.00	2.000	2.25	0.25	1.296	5.5694
5.25	2.025	2.30	0.275	1.425	5.3355
5.50	2.05	2.35	0.30	1.554	5.1022
5.75	2.10	2.45	0.35	1.812	4.8875
6.00	2.15	2.525	0.375	1.939	4.6562

$pk_1 = 6.25$ at $\bar{n} = 0.5$

$pk_2 = 5.20$ at $\bar{n} = 1.5$

$\underline{11.45}$

TABLE : 20 (d)

Metal-ligand stability constant at 25°C in 50% DMF $-H_2O$ system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.85	1.90	0.05	0.260	6.4594
4.25	1.925	2.025	0.10	0.519	6.2349
4.50	1.975	2.175	0.20	1.038	6.0398
5.00	2.00	2.25	0.25	1.296	5.5694
5.50	2.05	2.325	0.275	1.425	5.0859
5.75	2.10	2.425	0.325	1.682	4.8693
6.00	2.15	2.525	0.375	1.939	4.6562

$pk_1 = 6.25$ at $\bar{n} = 0.5$

$pk_2 = 5.05$ at $\bar{n} = 1.5$

11.30

TABLE : 21 (a)

Metal-ligand stability constant at 35°C in 50% DMF $-H_2O$ system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.75	1.80	1.85	0.05	0.260	6.6089
4.00	1.85	1.975	0.125	0.649	6.3973
4.25	1.95	2.125	0.175	0.908	6.1754
4.50	2.00	2.225	0.225	1.167	5.9547
4.75	2.075	2.35	0.275	1.425	5.7357
5.00	2.15	2.475	0.325	1.682	5.5185
5.25	2.20	2.550	0.350	1.812	5.2872
5.50	2.25	2.625	0.375	1.939	5.0561
5.75	2.30	2.70	0.400	2.068	4.8261

$pk_1 = 6.42$ at $\bar{n} = 0.5$

$pk_2 = 5.58$ at $\bar{n} = 1.5$

12.00

TABLE : 21 (b)

Metal-ligand stability constant at 35°C in 50% DMF $-H_2O$ **system with Ni(II).**

pH	V"	V"'	V"'-V"	$\bar{\bar{n}}$	pL
4.00	1.850	1.925	0.075	0.390	6.3716
4.25	1.950	2.050	0.100	0.519	6.1352
4.50	2.000	2.150	0.150	0.778	5.9119
4.75	2.075	2.275	0.200	1.038	5.6907
5.00	2.150	2.350	0.250	1.296	5.4702
5.25	2.200	2.500	0.300	1.554	5.2533
5.50	2.250	2.575	0.325	1.682	5.0202
5.75	2.300	2.650	0.350	1.812	4.7887
6.00	2.350	2.725	0.375	1.939	4.5583

$pk_1 = 6.17$ at $\bar{\bar{n}} = 0.5$

$pk_2 = \underline{5.29}$ at $\bar{\bar{n}} = 1.5$

$\underline{11.46}$

TABLE : 21 (c)

Metal-ligand stability constant at 35°C in 50% DMF -H_2O system with Co(II).

pH	V'	V''	V''-V'	$\bar{n}$	pL
4.00	1.85	1.900	0.050	0.260	6.3594
4.25	1.95	2.025	0.075	0.390	6.1225
4.50	2.00	2.100	0.100	0.519	5.8856
4.75	2.07	2.225	0.150	0.778	5.6650
5.00	2.15	2.325	0.175	0.908	5.4271
5.25	2.20	2.400	0.200	1.038	5.1920
5.50	2.25	2.500	0.250	1.296	4.9720
5.75	2.30	2.600	0.300	1.554	4.7549
6.00	2.35	2.700	0.350	1.812	4.5400

$pk_1 = 5.92$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.78}$ at $\bar{n} = 1.5$

$\underline{\underline{10.70}}$

TABLE : 21 (d)

Metal-ligand stability constant at 35°C in 50% DMF $-H_2O$ system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.95	2.000	0.050	0.260	6.1103
4.50	2.00	2.075	0.075	0.390	5.8729
4.75	2.075	2.175	0.100	0.519	5.6363
5.00	2.15	2.300	0.150	0.778	5.4133
5.25	2.20	2.400	0.200	1.038	5.1920
5.50	2.25	2.500	0.250	1.296	4.9720
5.75	2.30	2.575	0.275	1.425	4.7386
6.00	2.35	2.675	0.325	1.682	4.5225
6.25	2.40	2.775	0.375	1.939	4.3104

$pk_1 = 5.67$ at $\bar{n} = 0.5$

$pk_2 = 4.68$ at $\bar{n} = 1.5$

10.35

TABLE : 22 (a)

Metal-ligand stability constant at 45°C in 50% DMF $-H_2O$ system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
3.75	1.825	1.875	0.050	0.260	6.4592
4.00	1.850	1.950	0.100	0.519	6.2343
4.25	1.875	2.000	0.125	0.649	5.9976
4.50	1.900	2.075	0.175	0.908	5.7750
4.75	1.925	2.150	0.225	1.167	5.5542
5.00	1.975	2.225	0.250	1.296	5.3193
5.25	2.000	2.300	0.300	1.554	5.1018
5.50	2.050	2.375	0.325	1.682	4.8689
5.75	2.100	2.475	0.375	1.939	4.6558

$pk_1 = 6.16$ at $\bar{n} = 0.5$

$pk_2 = 5.14$ at $\bar{n} = 1.5$

$\overline{11.30}$

TABLE : 22 (b)

Metal-ligand stability constant at 45°C in 50% DMF $-H_2O$ system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.850	1.925	0.075	0.390	6.2216
4.25	1.875	2.000	0.125	0.649	5.9976
4.50	1.900	2.050	0.150	0.778	5.7612
4.75	1.925	2.100	0.175	0.908	5.5252
5.00	1.975	2.200	0.225	1.167	5.3047
5.25	2.000	2.275	0.275	1.425	5.0849
5.50	2.050	2.375	0.325	1.682	4.8689
5.75	2.100	2.475	0.375	1.939	4.6555
6.00	2.150	2.550	0.400	2.068	4.2660

$pk_1 = 6.12$ at $\bar{n} = 0.5$

$pk_2 = 5.01$ at $\bar{n} = 1.5$

11.13

TABLE : 22 (c)

Metal-ligand stability constant at 45°C in 50% DMF $-H_2O$ system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	1.850	1.900	0.050	0.260	6.2094
4.25	1.875	1.950	0.075	0.390	5.9719
4.50	1.900	2.025	0.125	0.649	5.7609
4.75	1.925	2.100	0.175	0.908	5.5252
5.00	1.975	2.200	0.225	1.167	5.3047
5.25	2.000	2.250	0.250	1.296	5.0698
5.50	2.050	2.325	0.275	1.425	4.8364
5.75	2.100	2.400	0.300	1.554	4.6030
6.00	2.150	2.500	0.350	1.812	4.3899

$pk_1 = 5.88$ at $\bar{n} = 0.5$

$pk_2 = 4.62$ at $\bar{n} = 1.5$

10.50

TABLE : 22 (d)

Metal-ligand stability constant at 45°C in 50% DMF -H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.875	1.950	0.075	0.390	5.9719
4.50	1.900	2.000	0.100	0.519	5.7348
4.75	1.925	2.075	0.150	0.778	5.5115
5.00	1.975	2.175	0.200	1.038	5.2900
5.25	2.000	2.225	0.225	1.167	5.0552
5.50	2.050	2.300	0.250	1.296	4.8206
5.75	2.100	2.400	0.300	1.554	4.6038
6.00	2.150	2.475	0.325	1.682	4.3717
6.25	2.200	2.550	0.350	1.812	4.1427

$pk_1 = 5.65$ at $\bar{n} = 0.5$

$pk_2 = 4.60$ at $\bar{n} = 1.5$

$\underline{\overline{10.25}}$

TABLE : 23 (a)

Metal-ligand stability constant at 25°C in 50% Acetonitrile-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.750	1.800	0.050	0.260	5.6183
4.50	1.800	1.900	0.100	0.520	5.3933
4.75	1.825	1.975	0.150	0.781	5.1696
5.00	1.850	2.050	0.200	1.039	4.9477
5.25	1.900	2.125	0.225	1.167	4.7126
5.50	1.975	2.225	0.250	1.297	4.4786
5.75	2.050	2.325	0.275	1.427	4.2467
6.00	2.100	2.400	0.300	1.556	4.0160
6.25	2.125	2.450	0.325	1.685	3.7879
6.50	2.175	2.525	0.350	1.814	3.5642
6.75	2.275	2.650	0.375	1.941	3.3473

$pk_1 = 5.45$ at $\bar{n} = 0.5$

$pk_2 = 4.25$ at $\bar{n} = 1.5$

$\overline{\underline{9.70}}$

TABLE : 23 (b)

Metal-ligand stability constant at 25°C in 50% Acetonitrile-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.750	1.775	0.025	0.130	5.6065
4.50	1.800	1.850	0.050	0.260	5.3688
4.75	1.825	1.925	0.100	0.520	5.1437
5.00	1.850	1.975	0.125	0.650	4.9069
5.25	1.900	2.075	0.175	0.909	4.6847
5.50	1.975	2.200	0.225	1.167	4.4641
5.75	2.050	2.300	0.250	1.297	4.2313
6.00	2.100	2.400	0.300	1.556	4.0160
6.25	2.125	2.475	0.350	1.814	3.8053
6.50	2.175	2.550	0.375	1.941	3.5816
6.75	2.275	2.675	0.400	2.071	3.3662

$pk_1 = 5.45$ at $\bar{n} = 0.5$

$pk_2 = 4.05$ at $\bar{n} = 1.5$

9.50

TABLE : 23 (c)

Metal-ligand stability constant at 25°C in 50% Acetonitrile-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.750	1.775	0.025	0.130	5.6065
4.50	1.800	1.875	0.075	0.390	5.3809
4.75	1.825	1.925	0.100	0.520	5.1437
5.00	1.850	1.975	0.125	0.650	4.9069
5.25	1.900	2.075	0.175	0.909	4.6847
5.50	1.975	2.175	0.200	1.039	4.4502
5.75	2.050	2.300	0.250	1.297	4.2313
6.00	2.100	2.375	0.275	1.427	3.9999
6.25	2.125	2.425	0.300	1.556	3.7712
6.50	2.175	2.500	0.325	1.685	3.5468
6.75	2.275	2.625	0.350	1.814	3.3299
7.00	2.350	2.725	0.375	1.941	3.1231

$pk_1 = 5.27$ at $\bar{n} = 0.5$

$pk_2 = 3.98$ at $\bar{n} = 1.5$

$\underline{\underline{9.25}}$

TABLE : 23 (d)

Metal-ligand stability constant at 25°C in 50% Acetonitrile-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.50	1.800	1.825	0.025	0.130	5.3688
4.75	1.825	1.900	0.075	0.390	5.1312
5.00	1.850	1.950	0.100	0.520	4.8941
5.25	1.900	2.025	0.125	0.650	4.6578
5.50	1.975	2.125	0.150	0.781	4.4225
5.75	2.050	2.250	0.200	1.039	4.2025
6.00	2.100	2.350	0.250	1.297	3.9844
6.25	2.125	2.425	0.300	1.556	3.7712
6.50	2.175	2.525	0.350	1.814	3.5642
6.75	2.275	2.650	0.375	1.941	3.3473
7.00	2.350	2.750	0.400	2.071	3.0820

$pk_1 = 4.95$ at $\bar{n} = 0.5$

$pk_2 = 3.95$ at $\bar{n} = 1.5$

$\underline{8.90}$

TABLE : 24 (e)

Metal-ligand stability constant at 35°C in 50% Acetonitrile-H_2O system with Cu(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.775	1.800	0.025	0.130	5.7667
4.50	1.800	1.850	0.050	0.260	5.5287
4.75	1.825	1.925	0.100	0.520	5.3035
5.00	1.850	1.975	0.125	0.650	5.0665
5.25	1.875	2.050	0.175	0.909	4.8440
5.50	1.925	2.125	0.200	1.039	4.6091
5.75	1.975	2.225	0.250	1.297	4.3895
6.00	2.000	2.300	0.300	1.556	4.1732
6.25	2.050	2.400	0.350	1.814	3.9612
6.50	2.100	2.500	0.400	2.071	3.7538

$pk_1 = 5.35$ at $\bar{n} = 0.5$

$pk_2 = 4.25$ at $\bar{n} = 1.5$

9.60

TABLE : 24 (b)

Metal-ligand stability constant at 35°C in 50% Acetonitrile-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.25	1.775	1.800	0.025	0.130	5.7667
4.50	1.800	1.850	0.050	0.260	5.5287
4.75	1.825	1.900	0.075	0.390	5.2911
5.00	1.850	1.975	0.125	0.650	5.0665
5.25	1.875	2.050	0.175	0.909	4.8440
5.50	1.925	2.175	0.250	1.297	4.6380
5.75	1.975	2.250	0.275	1.427	4.4050
6.00	2.000	2.325	0.325	1.685	4.1899
6.25	2.050	2.400	0.350	1.814	3.9612
6.50	2.100	2.475	0.375	1.941	3.7349

$pk_1 = 5.20$ at $\bar{n} = 0.5$

$pk_2 = \underline{4.20}$ at $\bar{n} = 1.5$

$\underline{9.40}$

TABLE : 24 (c)

Metal-ligand stability constant at 35°C in 50% Acetonitrile-H_2O system with Co(II).

pH	V''	V'''	V'''-V''	$\bar{n}$	pL
4.25	1.775	1.800	0.025	0.130	5.7667
4.50	1.800	1.850	0.050	0.260	5.5287
4.75	1.825	1.900	0.075	0.390	5.2911
5.00	1.850	1.950	0.100	0.520	5.0665
5.25	1.875	2.000	0.125	0.650	4.8173
5.50	1.925	2.075	0.150	0.781	4.5815
5.75	1.975	2.200	0.225	1.167	4.3745
6.00	2.000	2.275	0.275	1.427	4.1571
6.25	2.050	2.350	0.300	1.556	3.9271
6.50	2.100	2.450	0.350	1.814	3.7176

$pk_1 = 5.10$ at $\bar{n} = 0.5$

$pk_2 = 4.05$ at $\bar{n} = 1.5$

$\underline{\quad 9.15 \quad}$

TABLE : 24 (d)

Metal-ligand stability constant at 35°C in 50% Acetonitrile-$-H_2O$ system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{\bar{n}}$	pL
4.50	1.800	1.825	0.025	0.130	5.5169
4.75	1.825	1.875	0.050	0.260	5.2790
5.00	1.850	1.925	0.075	0.390	5.0415
5.25	1.875	2.000	0.125	0.650	4.8045
5.50	1.925	2.100	0.175	0.909	4.5951
5.75	1.975	2.200	0.225	1.167	4.3745
6.00	2.000	2.275	0.275	1.427	4.1771
6.25	2.050	2.375	0.325	1.685	3.9458
6.50	2.100	2.475	0.375	1.941	3.7349

$pk_1 = 4.80$ at $\bar{\bar{n}} = 0.5$

$pk_2 = \underline{4.00}$ at $\bar{\bar{n}} = 1.5$

$\underline{8.80}$

TABLE : 25 (a)

Metal-ligand stability constant at 45°C in 50% Acetonitrile-$-H_2O$ system with Cu(II)

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.50	1.675	1.700	0.025	0.130	5.4159
4.75	1.700	1.750	0.050	0.260	5.1780
5.00	1.725	1.800	0.075	0.390	4.9405
5.25	1.775	1.900	0.125	0.650	4.7166
5.50	1.825	2.000	0.175	0.909	4.4946
5.75	1.900	2.100	0.200	1.039	4.2606
6.00	1.950	2.200	0.250	1.297	4.0423
6.25	2.025	2.225	0.300	1.556	3.8289
6.50	2.075	2.400	0.325	1.685	3.6035
6.75	2.125	2.475	0.350	1.814	3.3847

$pk_1 = 4.84$ at $\bar{n} = 0.5$

$pk_2 = \underline{3.88}$ at $\bar{n} = 1.5$

$\underline{8.72}$

TABLE : 25 (b)

Metal-ligand stability constant at 45°C in 50% Acetonitrile-H_2O system with Ni(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.50	1.675	1.700	0.025	0.130	5.4159
4.75	1.700	1.750	0.050	0.260	5.1780
5.00	1.725	1.800	0.075	0.390	4.9405
5.25	1.775	1.875	0.100	0.520	4.7039
5.50	1.825	1.975	0.150	0.781	4.4810
5.75	1.900	2.075	0.175	0.909	4.2466
6.00	1.950	2.175	0.225	1.167	4.0273
6.25	2.025	2.300	0.275	1.427	3.8128
6.50	2.075	2.400	0.325	1.685	3.6055

$pk_1 = 4.75$ at $\bar{n} = 0.5$

$pk_2 = 3.75$ at $\bar{n} = 1.5$

8.50

TABLE : 25 (c)

Metal-ligand stability constant at 45°C in 50% Acetonitrile-H_2O system with Co(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.75	1.700	1.725	0.025	0.130	5.1663
5.00	1.725	1.775	0.050	0.260	4.9284
5.25	1.775	1.850	0.075	0.390	4.6914
5.50	1.825	1.925	0.100	0.520	4.4550
5.75	1.900	2.050	0.150	0.781	4.2329
6.00	1.950	2.200	0.250	1.297	4.0425
6.25	2.025	2.300	0.275	1.427	3.8128
6.50	2.075	2.400	0.325	1.685	3.6035
6.75	2.125	2.500	0.375	1.941	3.4017

$pk_1 = 4.50$ at $\bar{n} = 0.5$

$pk_2 = \underline{3.80}$ at $\bar{n} = 1.5$

$\underline{8.30}$

TABLE : 25 (d)

Metal-ligand stability constant at 45°C in 50% Acetonitrile-H_2O system with Fe(II).

pH	V"	V"'	V"'-V"	$\bar{n}$	pL
4.75	1.700	1.725	0.025	0.130	5.1663
5.00	1.725	1.775	0.050	0.260	4.9284
5.25	1.775	1.850	0.075	0.390	4.6914
5.50	1.825	1.950	0.125	0.650	4.4678
5.75	1.900	2.075	0.175	0.901	4.2745
6.00	1.950	2.175	0.225	1.167	4.0273
6.25	2.025	2.275	0.250	1.297	3.7973
6.50	2.075	2.375	0.300	1.556	3.5868
6.75	2.125	2.475	0.350	1.814	3.3843

$pk_1 = 4.55$ at $\bar{n} = 0.5$

$pk_2 = 3.55$ at $\bar{n} = 1.5$

$\overline{8.10}$

Proton-Ligand Stability Constant of PAP in different solvents.

(all are in 50% solvent $-H_2O$ mixture)

	Methanol	Ethanol	Iso-propanol	DFM	Acetonitrile
logpKH at 25°C	8.01	8.31	8.39	8.42	7.99
35°C	7.98	8.295	8.32	8.32	7.89
45°C	7.94	8.065	8.13	8.17	7.83
pkH at 25°C	1.02×10^8	2.04×10^8	2.45×10^8	2.63×10^8	9.77×10^7
35°C	9.55×10^7	1.97×10^8	2.09×10^8	2.09×10^8	7.76×10^7
45°C	8.71×10^7	1.16×10^8	1.35×10^8	1.48×10^8	6.76×10^7

TABLE : 27

Metal-ligand stability constants of the complexes.

		50% Methanol $-H_2O$			50% Ethanol $-H_2O$			50% Iso-propanol $-H_2O$			50% DMF $-H_2O$			50% Acetonitrile $-H_2O$		
		25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Cu(II)	$\log k_1$	5.65	5.80	5.30	7.15	6.35	6.15	6.60	6.50	6.20	6.58	6.42	6.16	5.45	5.35	4.75
	$\log k_2$	4.45	3.80	4.25	4.15	4.15	3.80	5.80	5.50	5.10	5.52	5.58	5.14	4.25	4.25	3.75
	$\log \beta$	10.10	9.60	9.55	11.30	10.50	9.95	12.40	12.00	11.30	12.10	12.00	11.30	9.70	9.60	8.50
Ni(II)	$\log k_1$	5.40	5.85	5.10	6.65	6.125	5.70	6.30	6.15	5.95	6.38	6.17	6.12	5.45	5.20	4.84
	$\log k_2$	4.45	3.55	4.10	4.30	3.875	4.20	5.25	5.05	4.85	5.44	5.29	5.01	4.05	4.20	3.88
	$\log \beta$	9.85	9.40	9.20	10.95	10.00	9.90	11.55	11.20	10.80	11.82	11.46	11.13	9.50	9.40	8.70
Co(II)	$\log k_1$	5.30	4.85	4.85	7.05	5.25	5.15	6.20	6.00	4.70	6.25	5.92	5.88	5.27	5.10	4.50
	$\log k_2$	4.30	4.10	3.50	3.65	4.50	4.30	4.85	4.80	5.70	5.20	4.78	4.62	3.98	4.05	3.80
	$\log \beta$	9.60	8.95	8.35	10.70	9.75	9.45	11.05	10.80	10.40	11.45	10.70	10.50	9.25	9.15	8.30
Fe(II)	$\log k_1$	5.05	5.05	4.60	5.65	5.875	5.40	6.25	5.90	5.70	6.25	5.67	5.65	4.95	4.80	4.55
	$\log k_2$	4.15	3.85	3.55	4.55	3.65	3.37	4.65	4.65	4.60	5.05	4.68	4.60	3.95	4.00	3.60
	$\log \beta$	9.20	8.90	8.15	10.20	9.525	8.75	10.90	10.55	10.30	11.30	10.35	10.25	8.90	8.80	8.15

TABLE : 28 (a)

Change of free energy (ΔG) in Kcal. mole^{-1} of the complexes.

		50% Methanol $-H_2O$			50% Ethanol $-H_2O$			50% Iso-propanol $-H_2O$			50% DMF $-H_2O$			50% Acetonitrile $-H_2O$		
		25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Cu(II)	$\log k_1$	− 7.704	− 8.175	− 7.712	− 9.750	− 8.949	− 8.949	− 9.000	− 9.161	− 9.022	− 8.973	− 9.048	− 8.964	− 7.434	− 7.540	−6.912
	$\log k_2$	− 6.068	− 5.356	− 6.184	− 5.659	− 5.849	− 5.530	− 7.909	− 7.752	− 7.421	− 7.527	− 7.865	− 7.479	− 5.796	− 5.990	− 5.457
	$\log \beta$	−13.772	−13.531	−13.896	−15.409	−14.798	−14.479	−16.909	−16.913	−16.443	−16.500	−16.913	−16.443	−13.228	−13.530	−12.369
Ni(II)	$\log k_1$	− 7.364	− 8.245	− 7.421	− 9.068	− 8.667	− 8.294	− 8.591	− 8.668	− 8.658	− 8.700	− 8.696	− 8.906	− 7.432	− 7.329	− 7.043
	$\log k_2$	− 6.068	− 5.003	− 5.778	− 5.864	− 5.427	− 6.112	− 7.159	− 7.117	− 7.057	− 7.418	− 7.456	− 7.290	− 5.523	− 5.919	− 5.646
	$\log \beta$	−13.432	−13.248	−13.199	−14.932	−14.094	−14.406	−15.750	−15.785	−15.715	−16.118	−16.152	−16.196	−12.975	−13.248	−12.689
Co(II)	$\log k_1$	− 7.227	− 6.835	− 7.057	− 9.614	− 7.399	− 7.494	− 8.455	− 8.456	− 6.839	− 8.523	− 8.344	− 8.556	− 7.186	− 7.188	− 6.548
	$\log k_2$	− 5.863	− 5.778	− 5.093	− 4.977	− 6.342	− 6.257	− 6.614	− 6.765	− 8.294	− 7.091	− 6.737	− 6.723	− 5.427	− 5.708	− 5.529
	$\log \beta$	−13.090	−12.614	−12.150	−14.591	−13.741	−13.751	−15.069	−15.221	−15.133	−15.614	−15.081	−15.279	−12.613	−12.896	−12.077
Fe(II)	$\log k_1$	− 6.886	− 7.117	− 6.693	− 7.704	− 8.245	− 7.858	− 8.525	− 8.316	− 8.294	− 8.523	− 7.991	− 8.222	− 6.750	− 6.765	− 6.621
	$\log k_2$	− 5.659	− 5.426	− 5.166	− 6.205	− 5.144	− 4.874	− 6.341	− 6.554	− 6.694	− 6.886	− 6.596	− 6.694	− 5.386	− 5.638	− 5.238
	$\log \beta$	−12.545	−12.543	−11.859	−13.909	−13.389	−12.732	−14.864	−14.870	−14.988	−15.409	−14.587	−14.916	−12.136	−12.403	−11.859

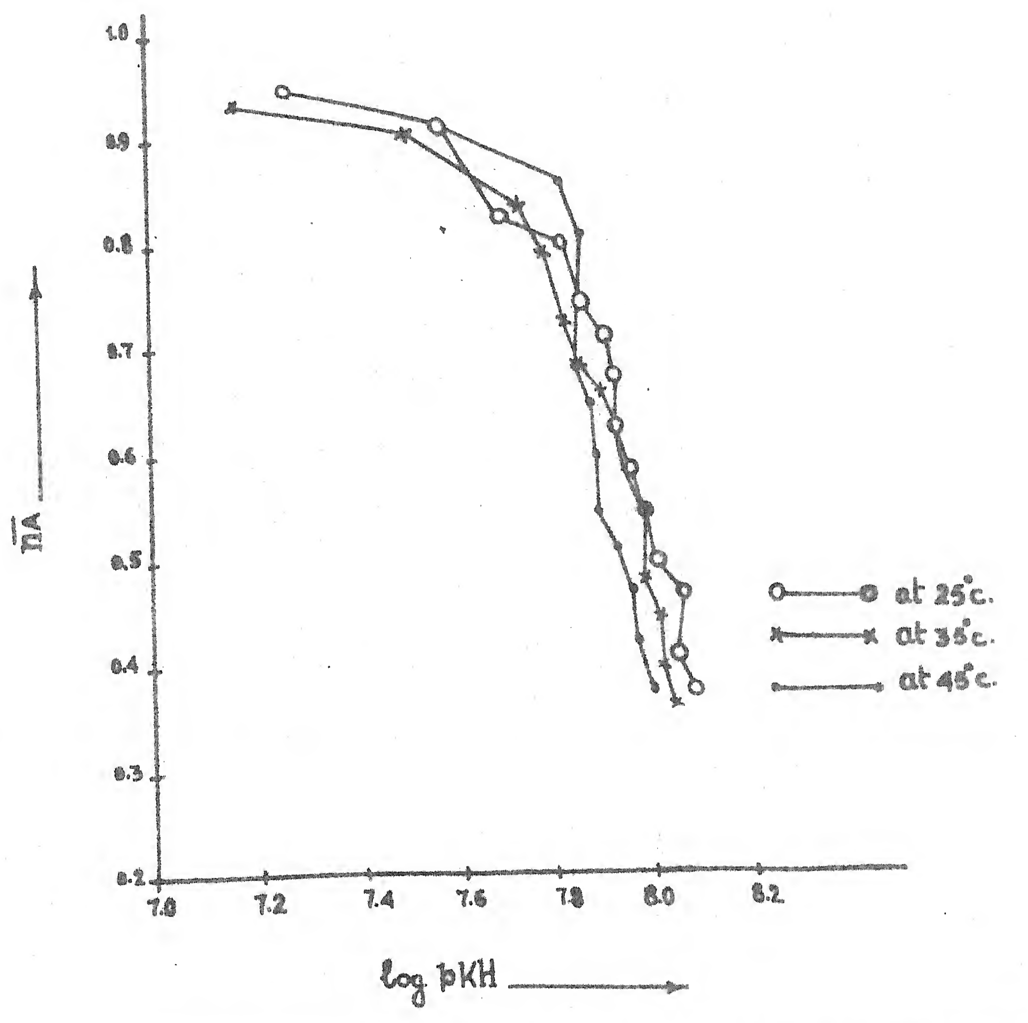
TABLE : 28 (b)

Change in Enthalpy (ΔH) in Kcals. for temperature difference of 10°C.

(all in 50% solvent $-H_2O$ mixture)

	Methanol	Ethanol	Iso-propanol	DMF	Acetonitrile
Cu(II) log β	- 4.395	-11.143	- 7.295	- 1.825	-21.407
Ni(II) log β	- 3.355	-15.283	- 6.383	- 6.565	-13.254
Co(II) log β	- 8.681	-15.501	- 4.559	-13.678	-16.542
Fe(II) log β	- 0.036	- 9.483	- 6.383	-17.326	-12.649

FIG. - 6



IN 50% METHANOL - H_2O SYSTEM PROTON- LIGAND STABILITY CONST OF PAP.

PROTON. LIGAND STABILITY CONST OF PAP IN 50% ETHANOL. H_2O SYSTEM.

FIG. 7.

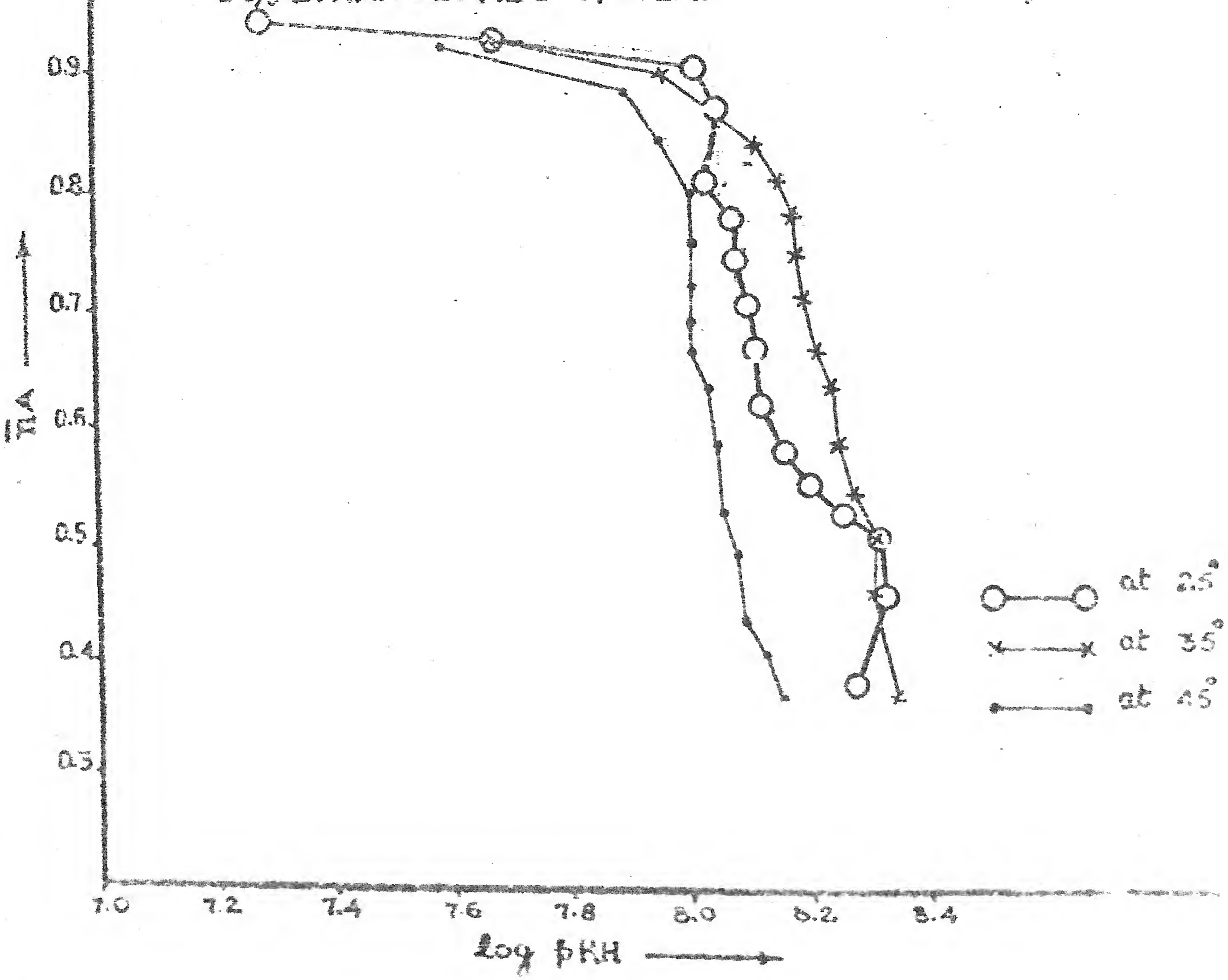


FIG. 8

PROTON - LIGAND STABILITY CONST OF PAP IN 50% ISO-PROPANOL-H_2O SYSTEM

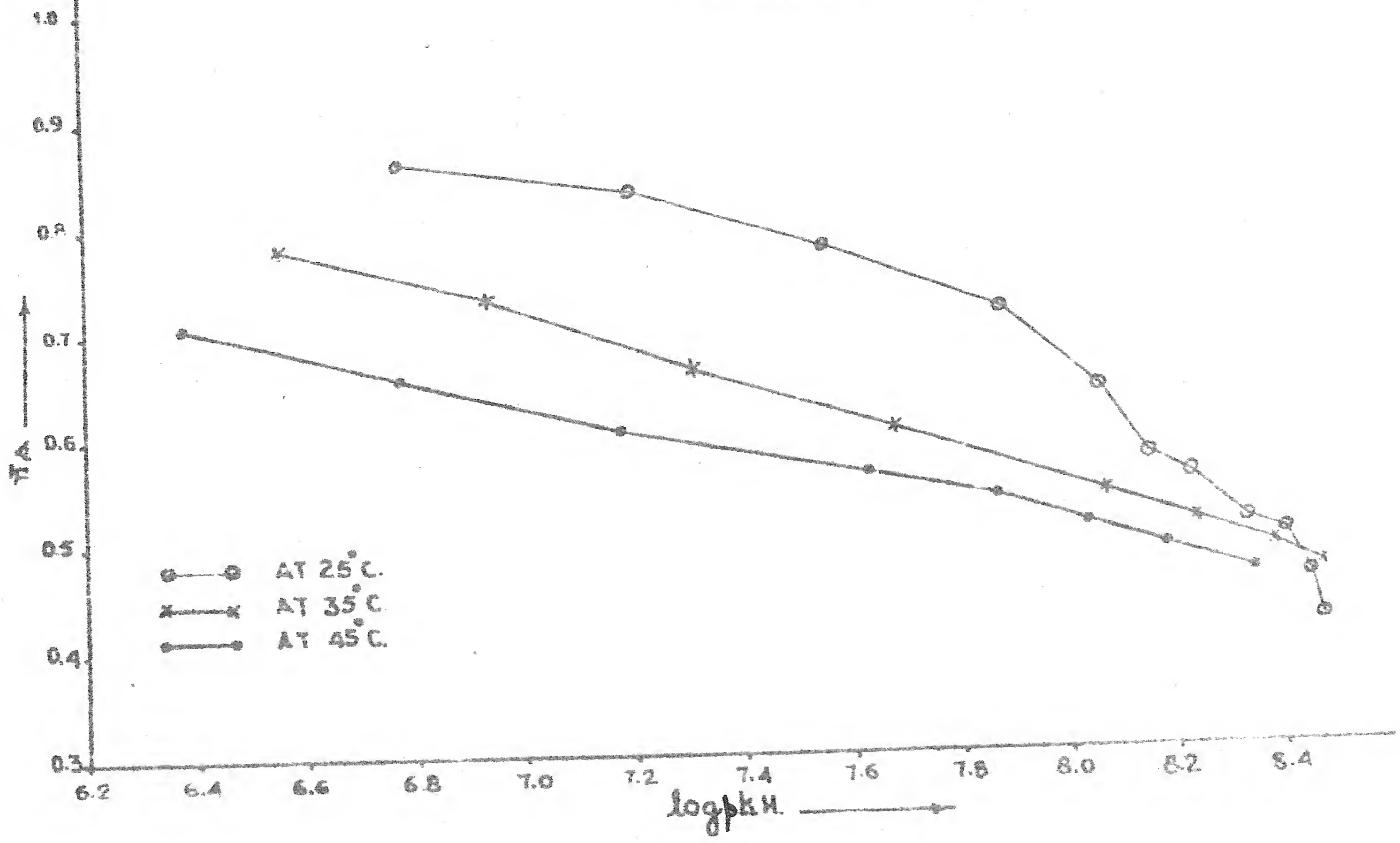


FIG. 9

Proton-Ligand Stability Const. of FAP in 50% DMF-H_2O System.

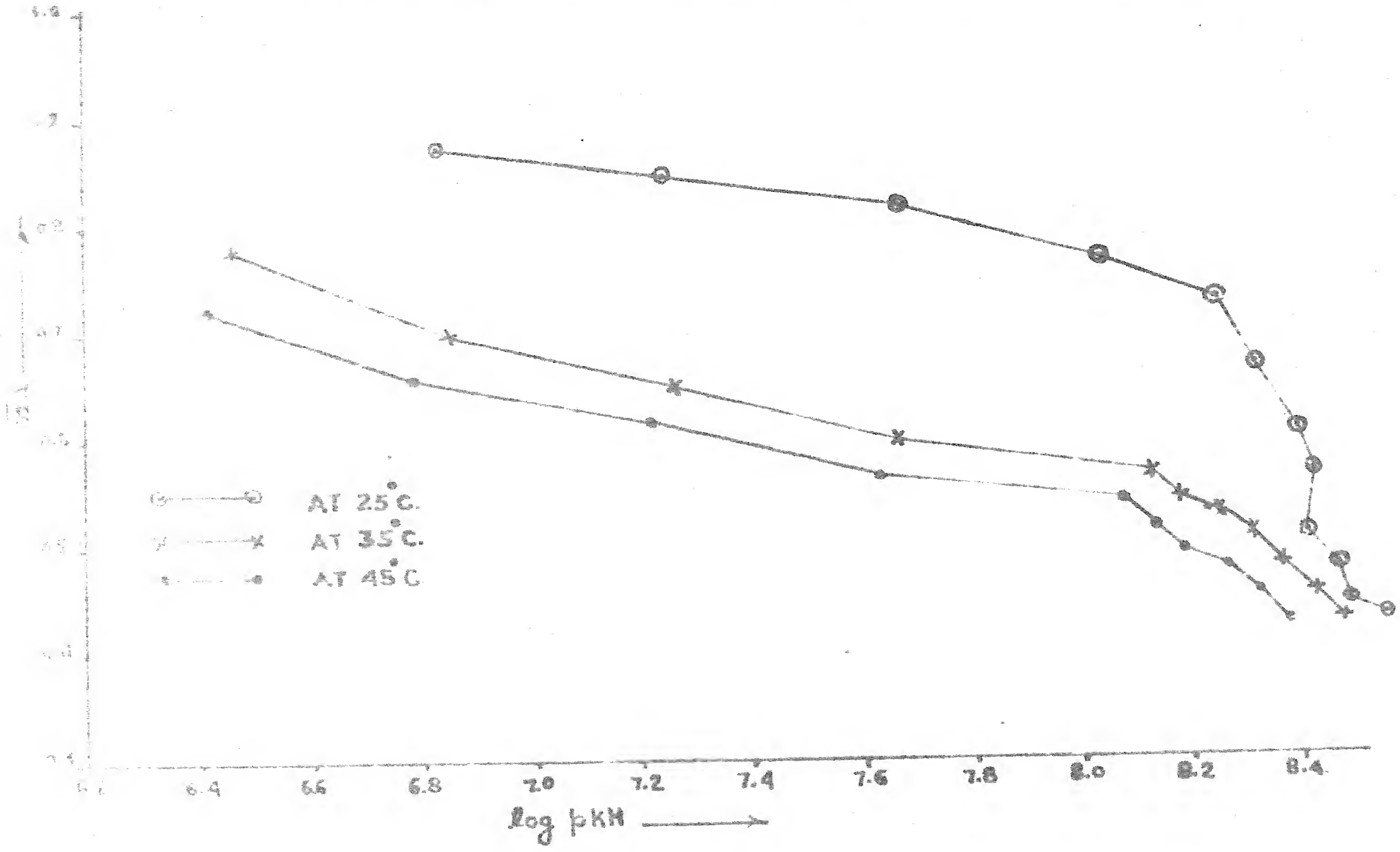


FIG. 10.

PROTON-LIGAND STABILITY CONSTANT OF PAP IN 50% ACETONITRILE-H_2O SYSTEM.

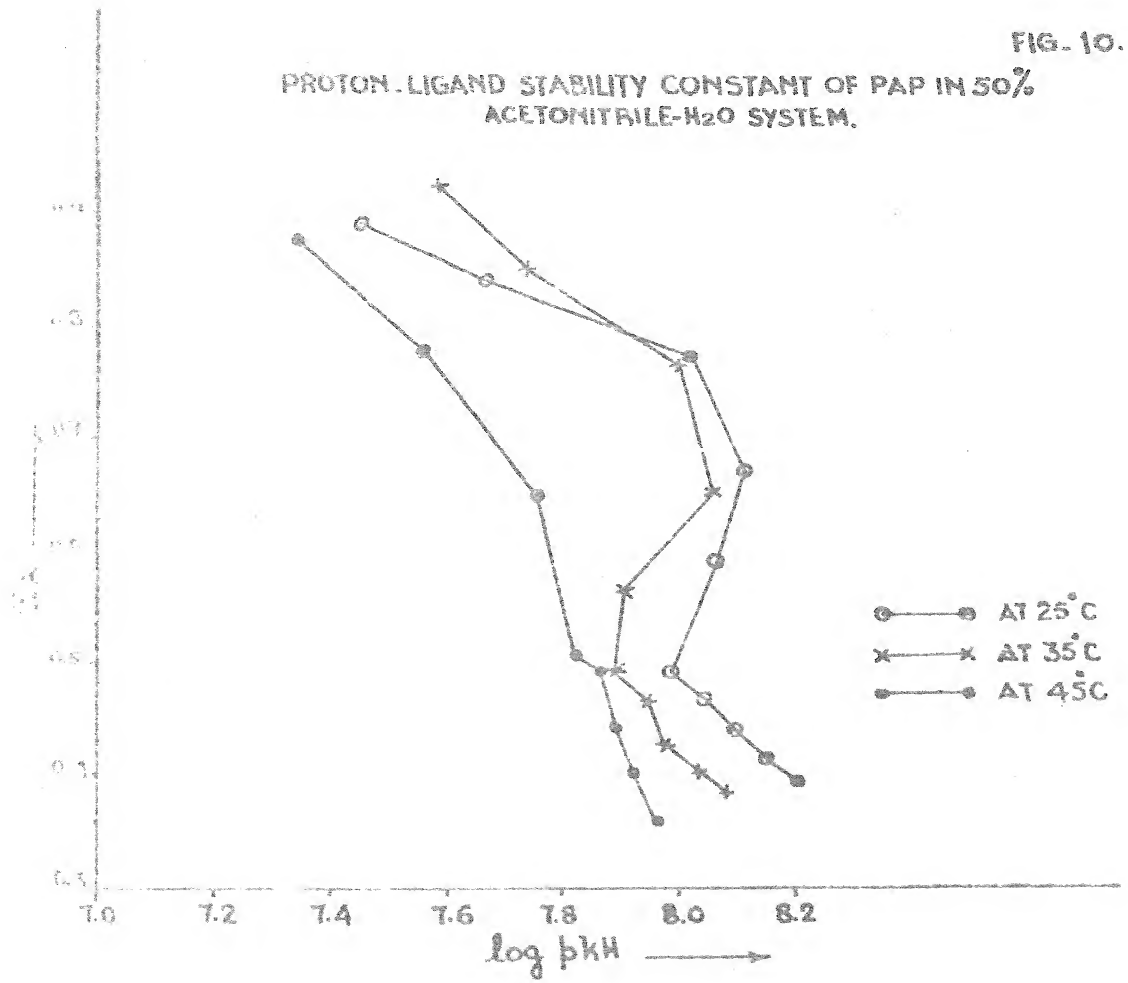


FIG.- 11 (a)

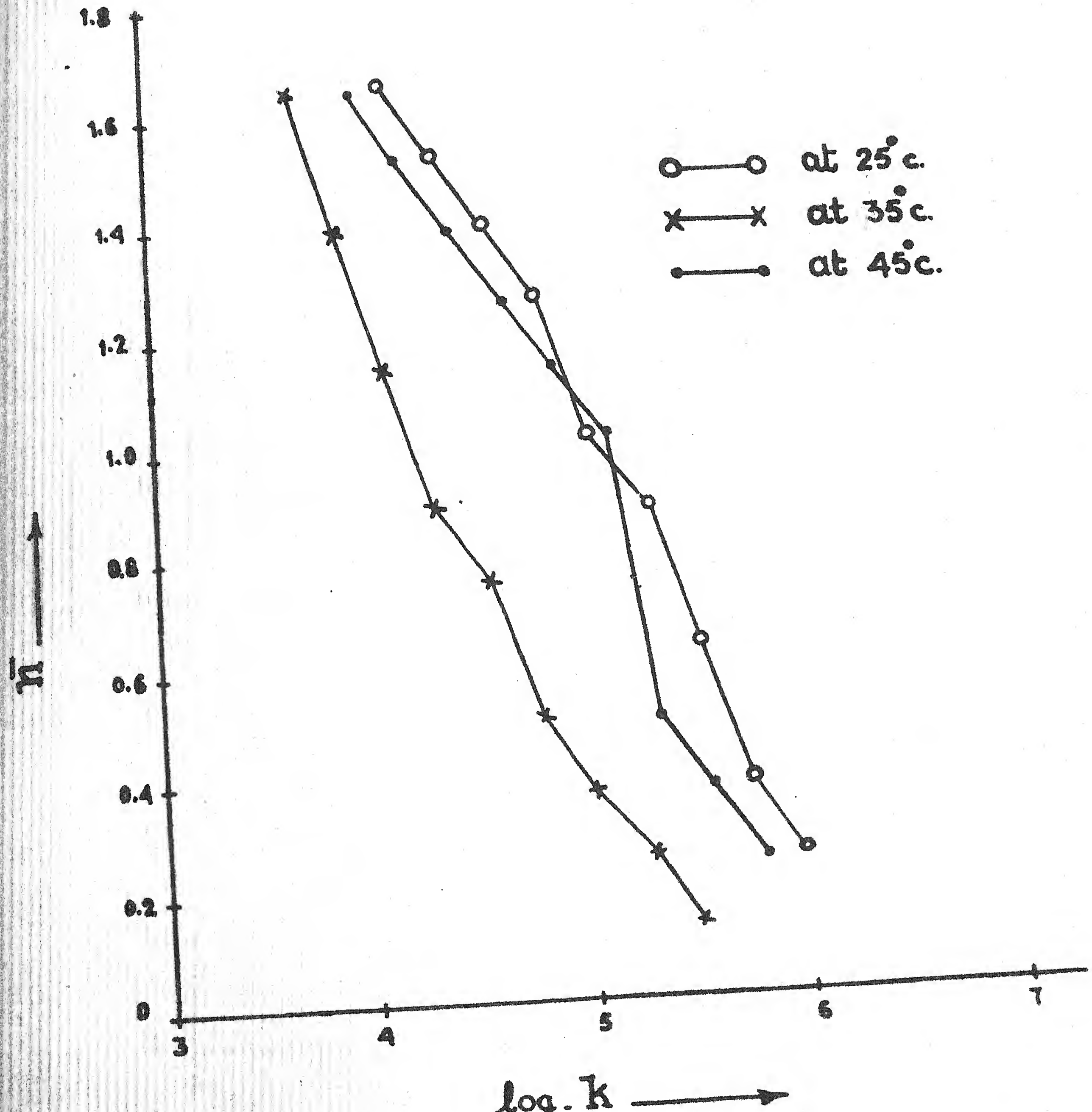


FIG. - 11 (b)

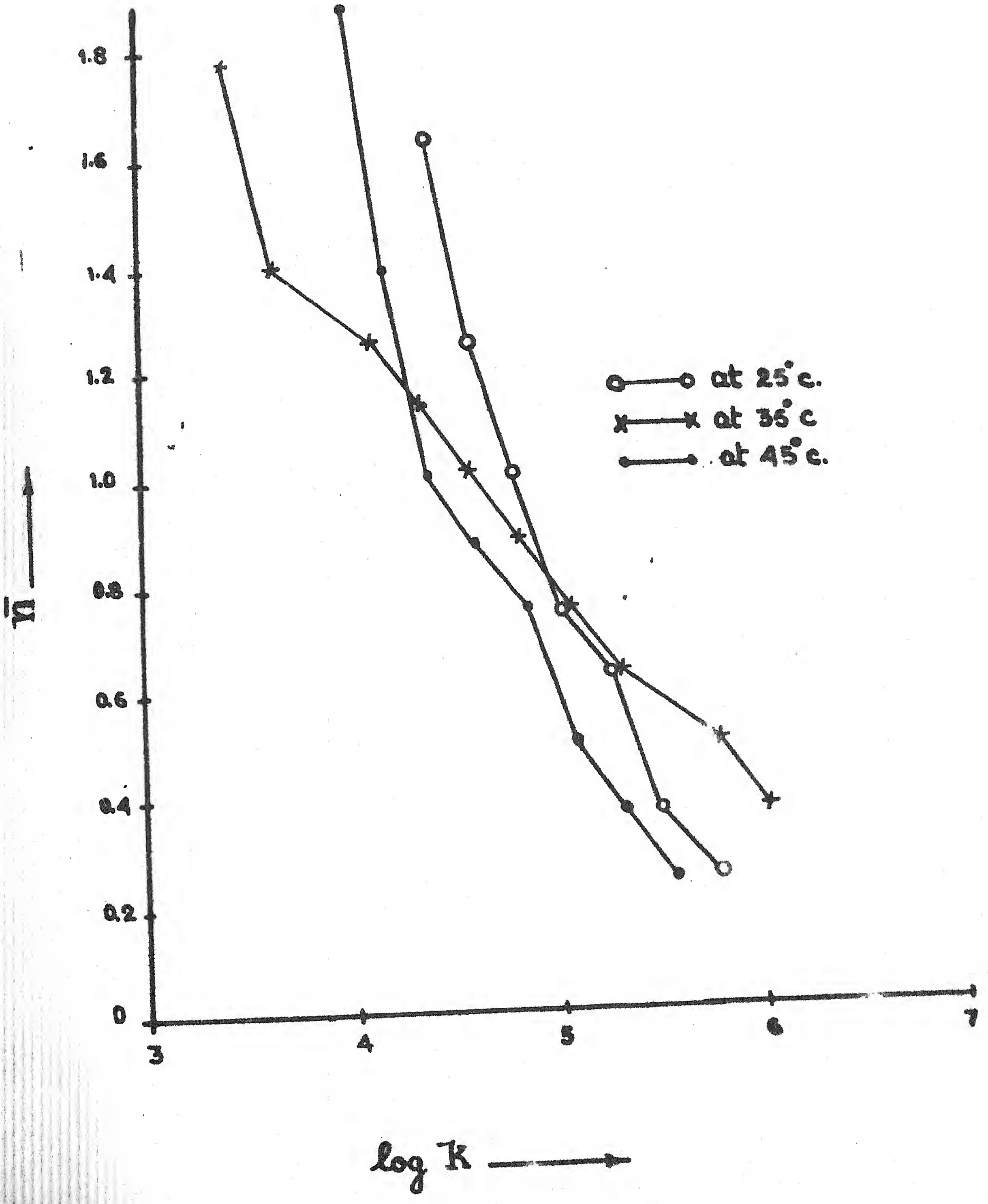


FIG.- 11 (c)

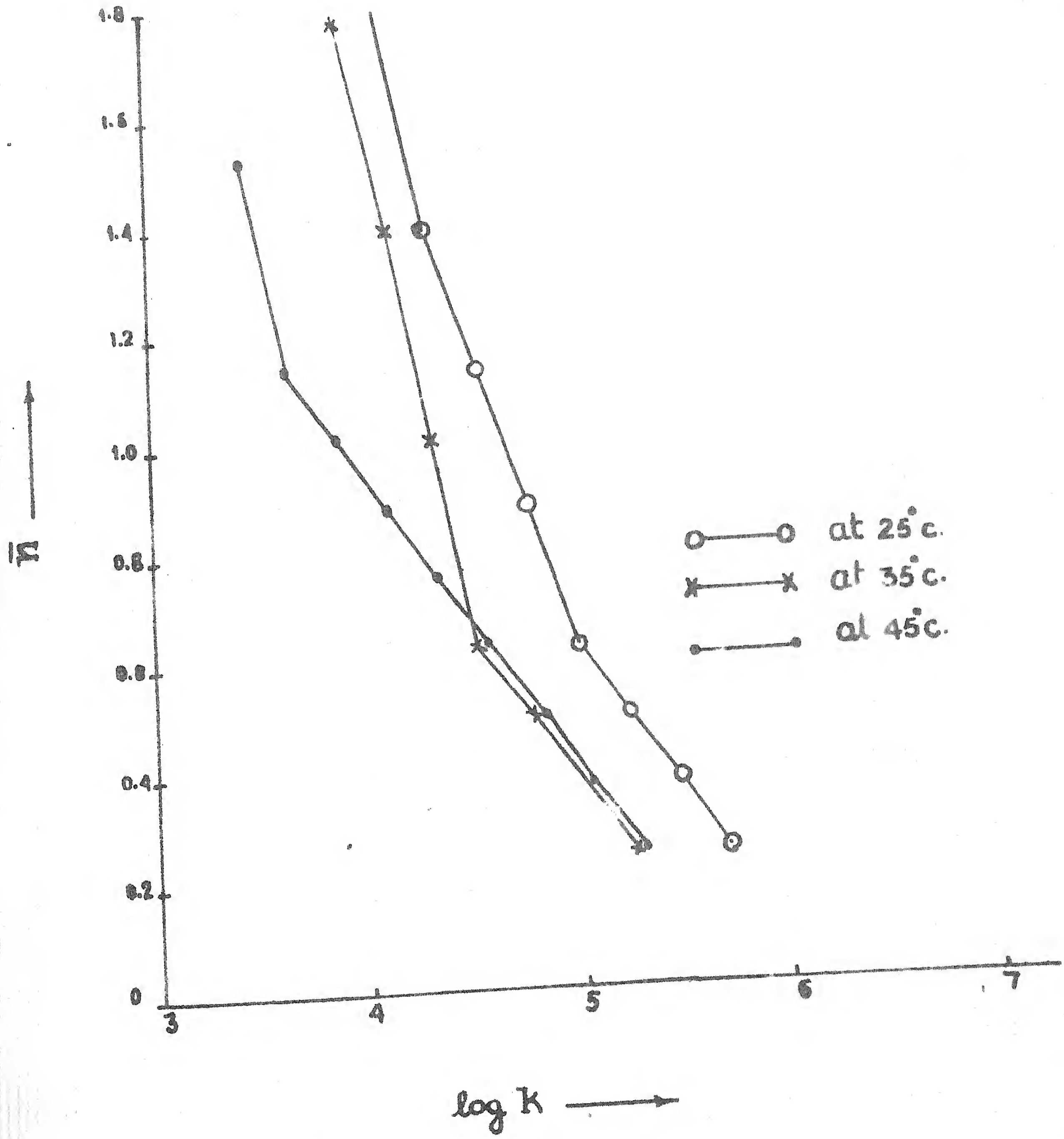
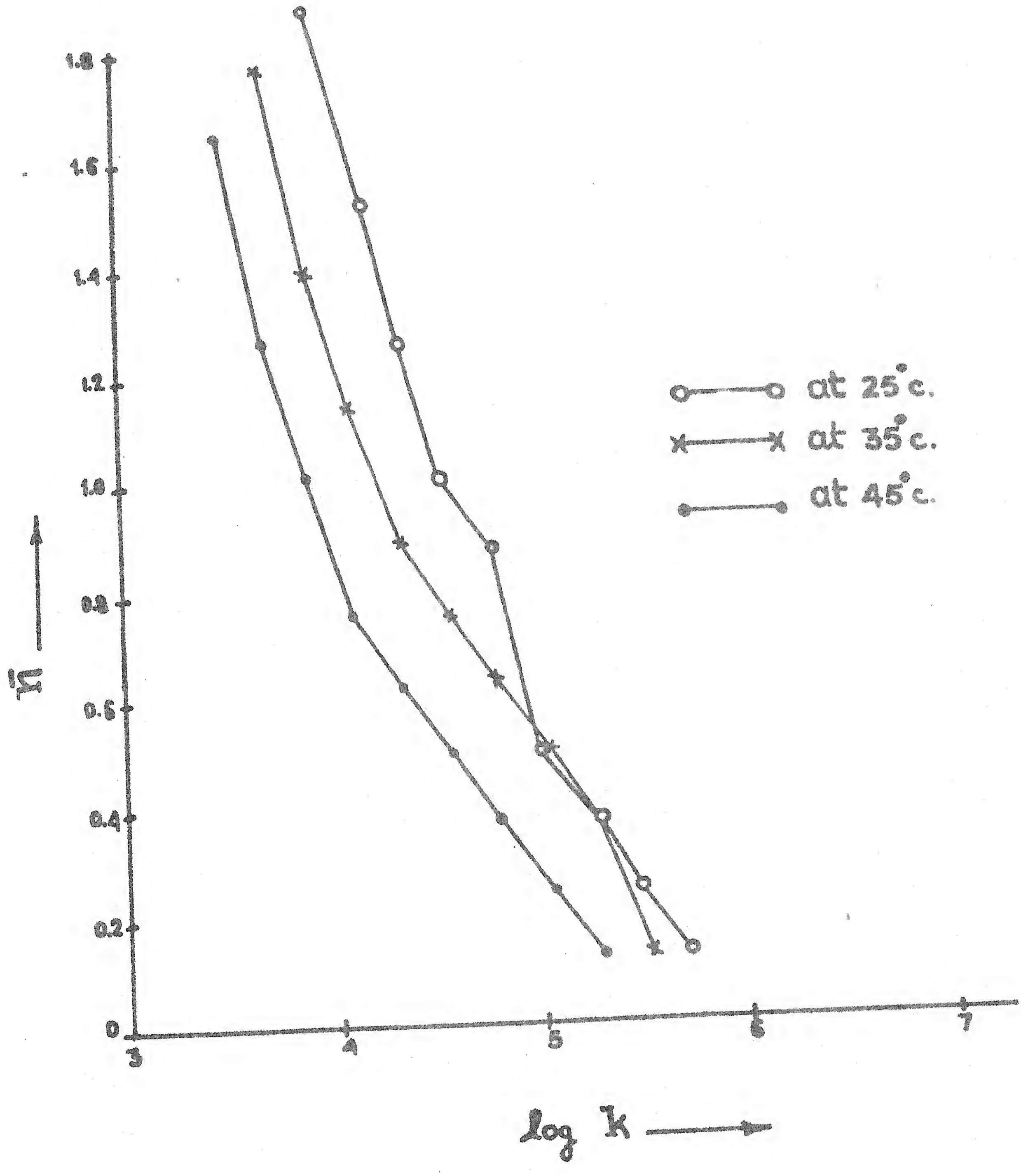


FIG. - 11 (d)



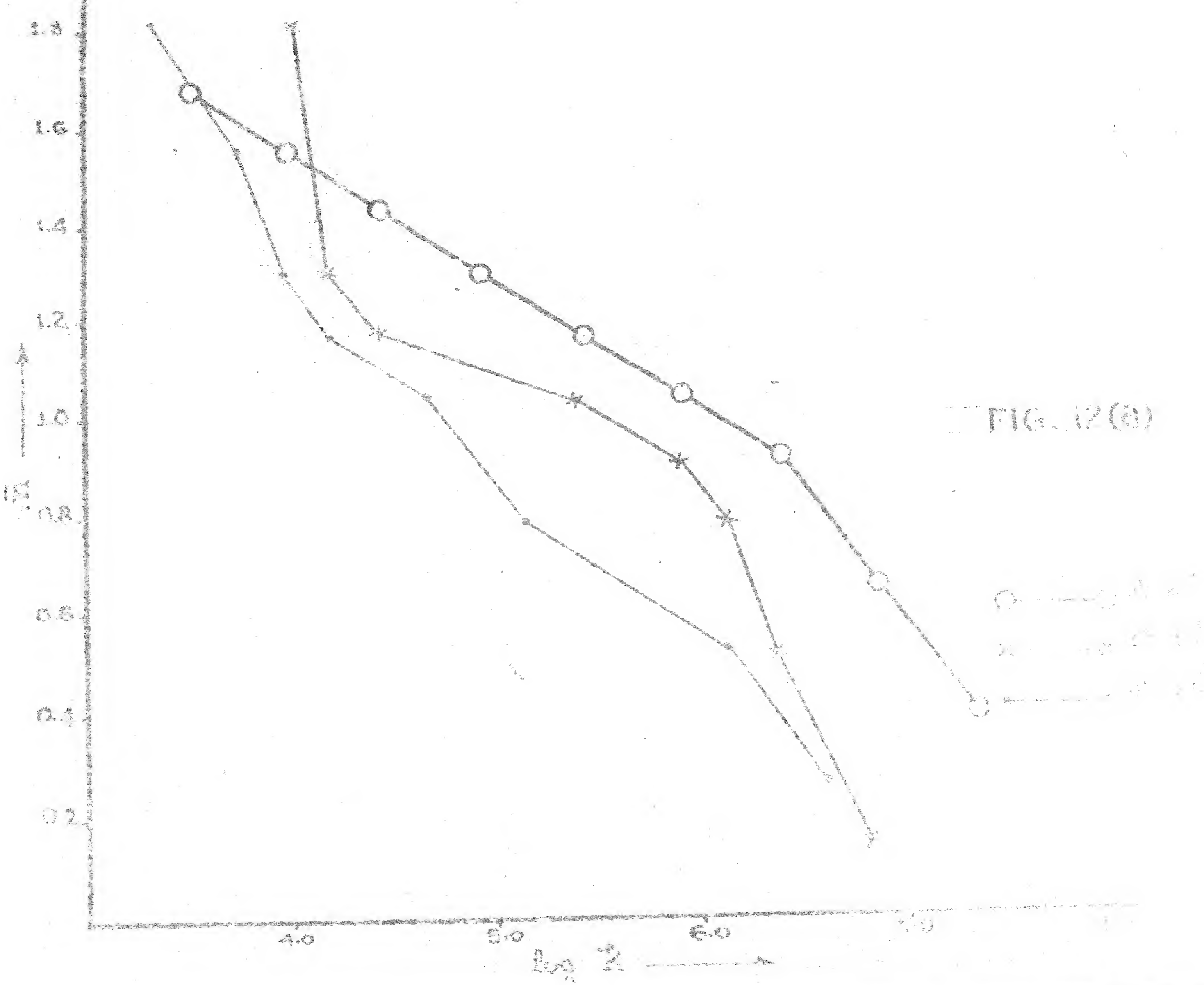


FIG. 12(6)

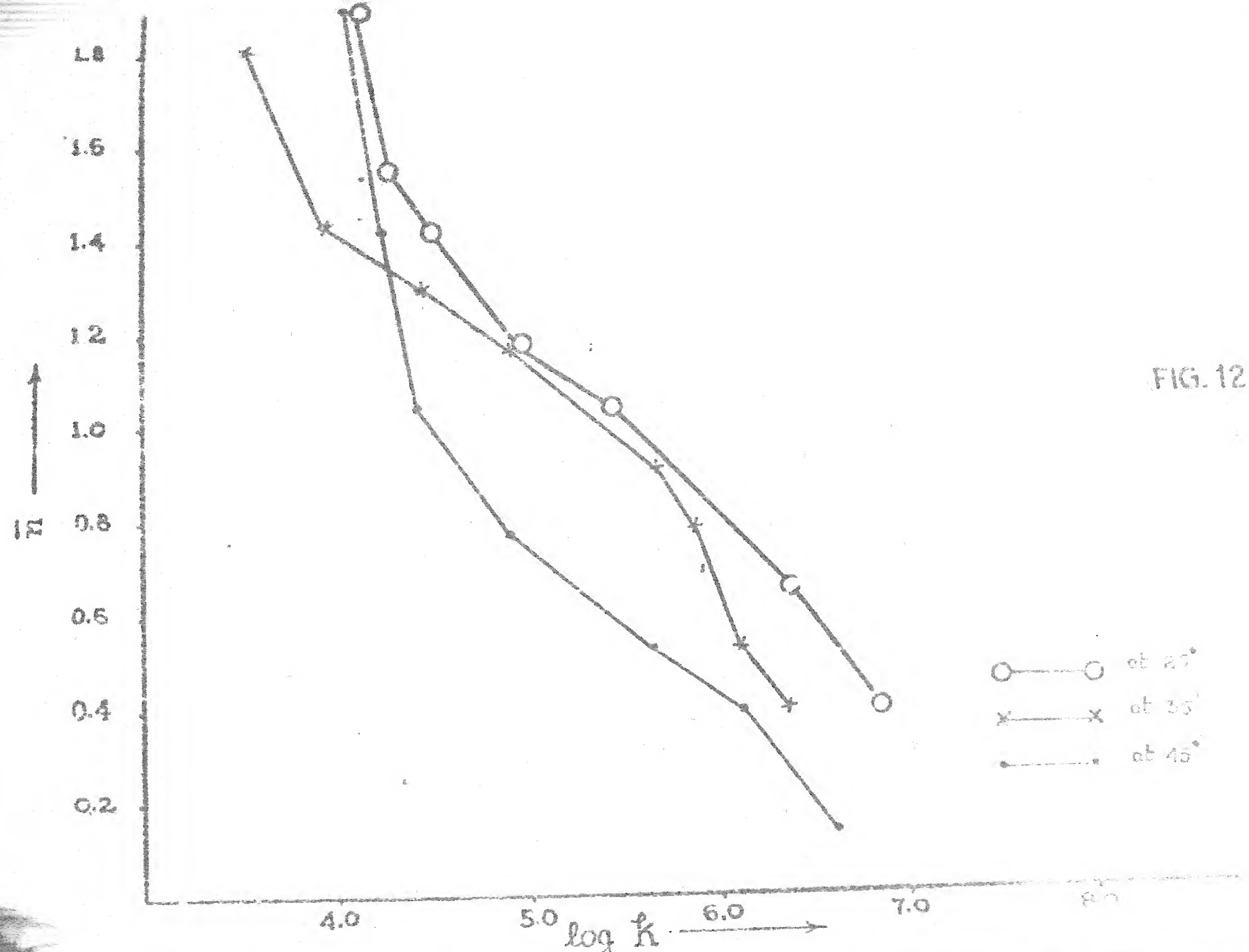


FIG. 12 (b)

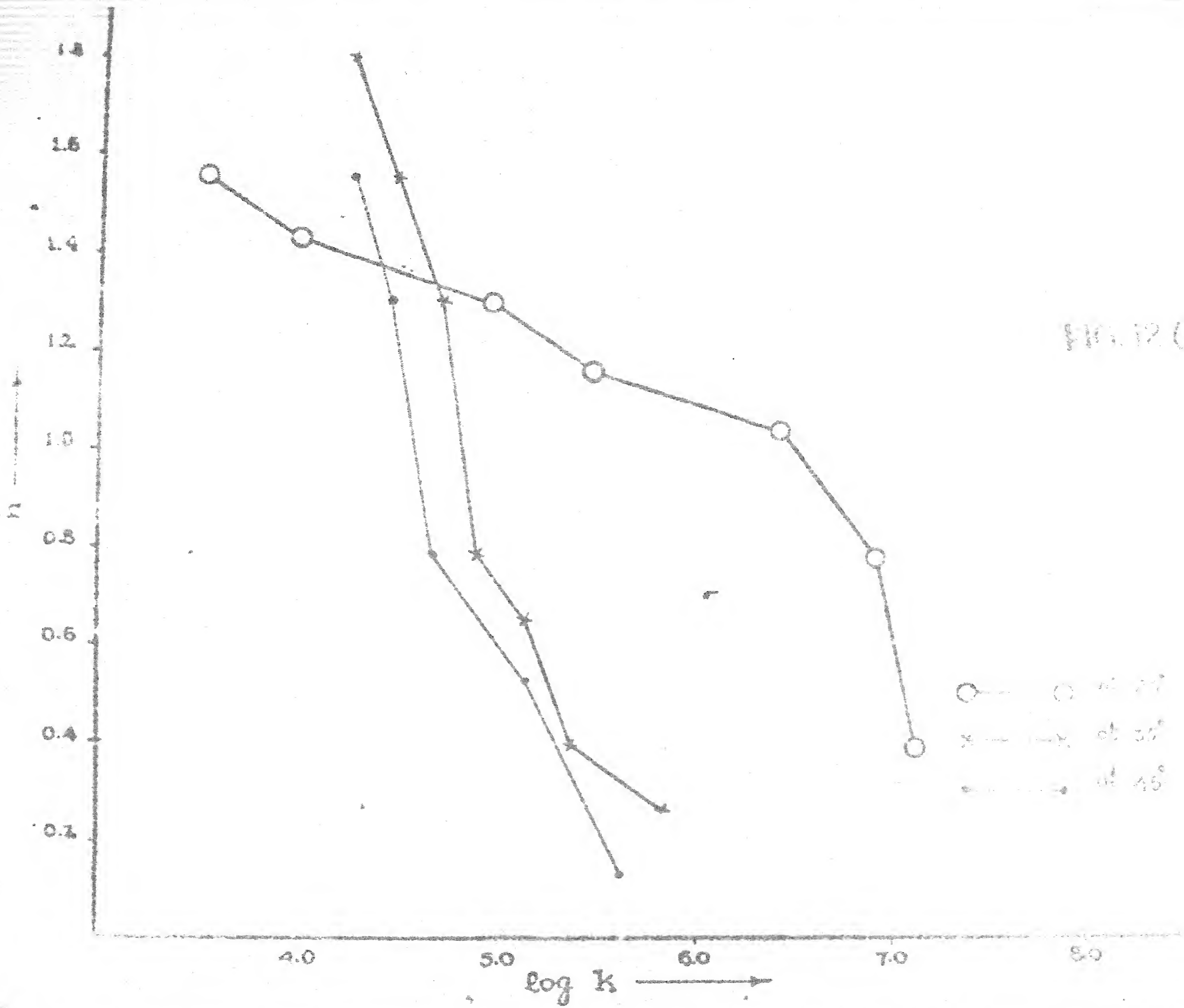


FIG. 12 (c)

FIG. 12(d)

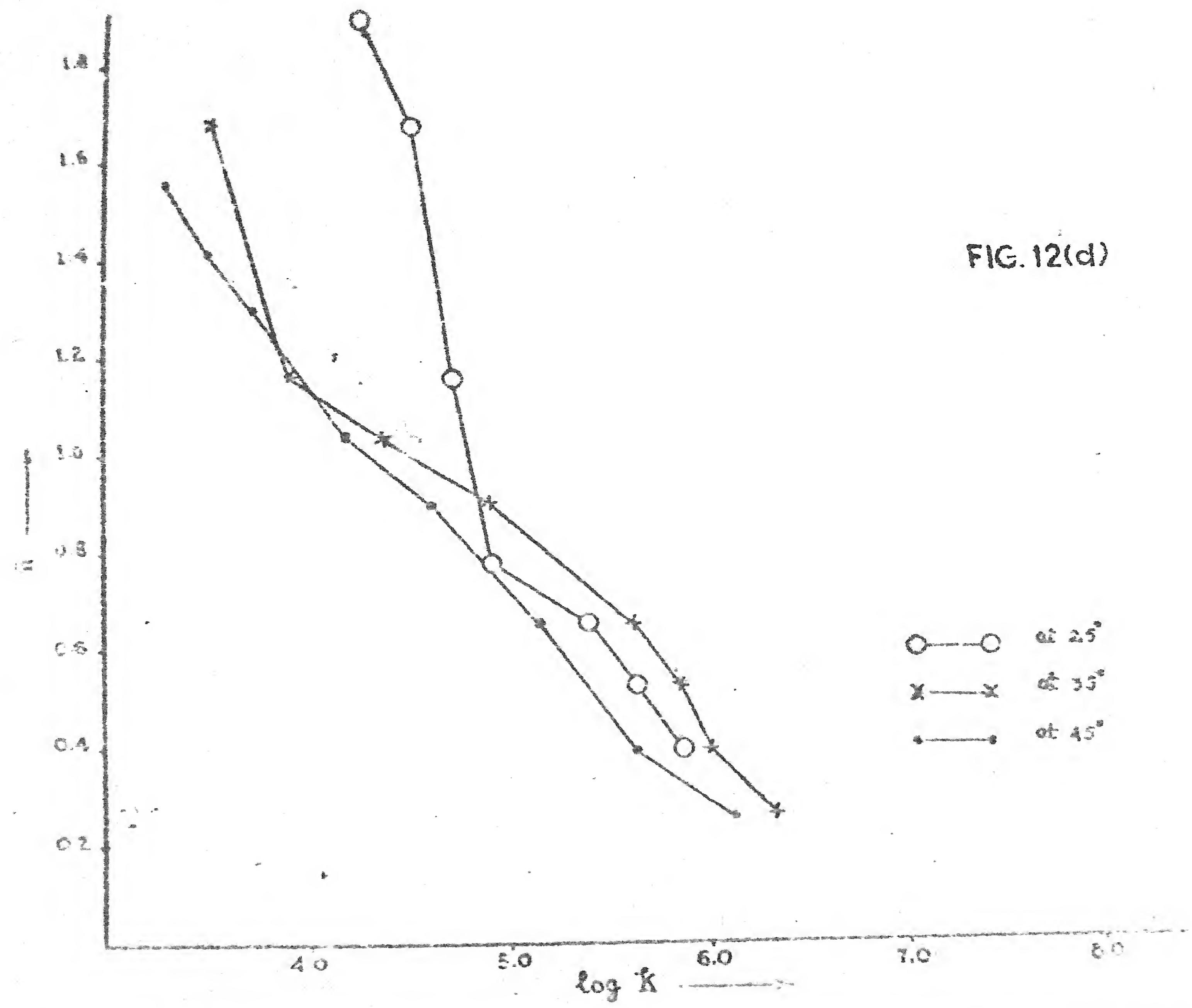


FIG. 13 (a)

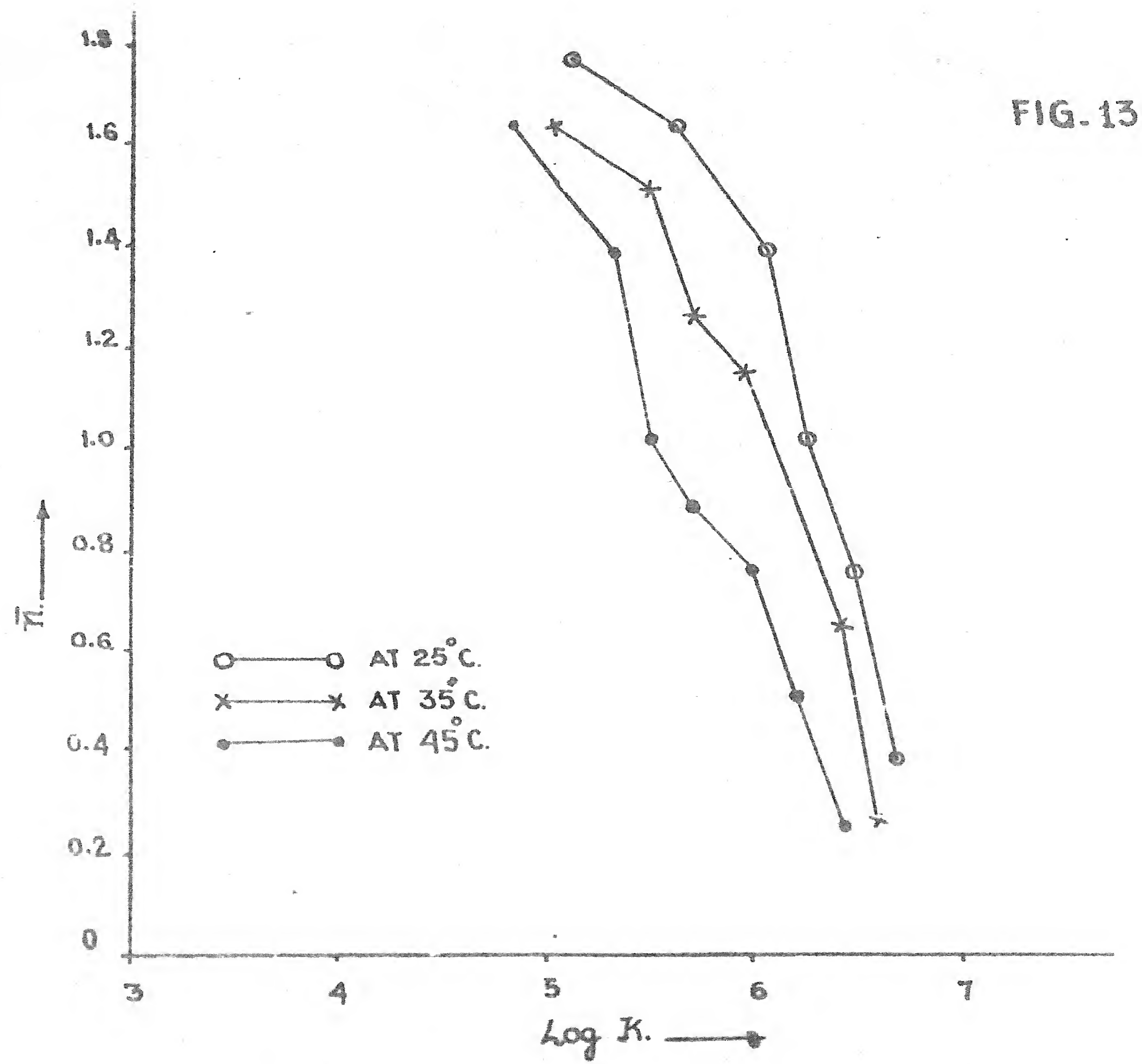
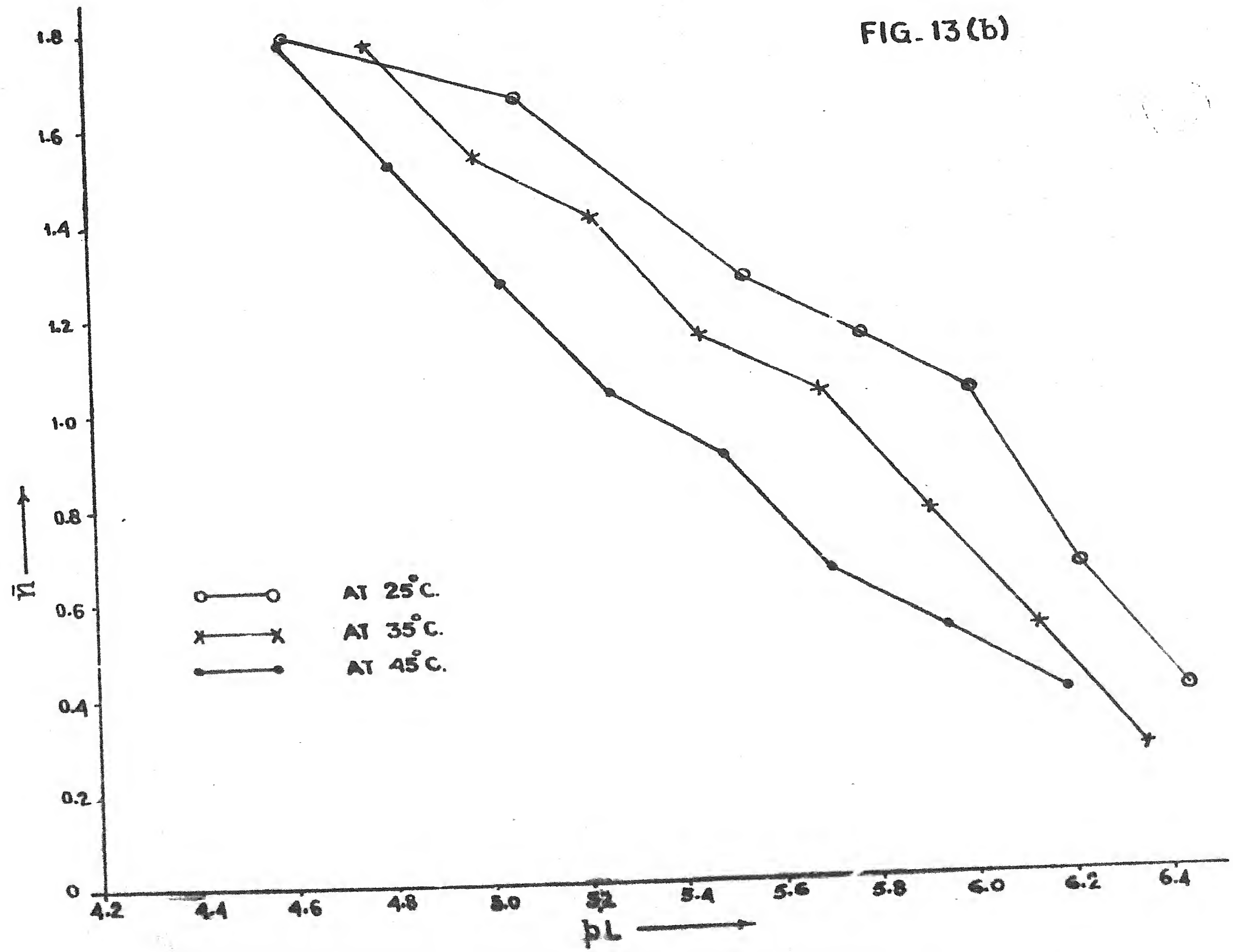
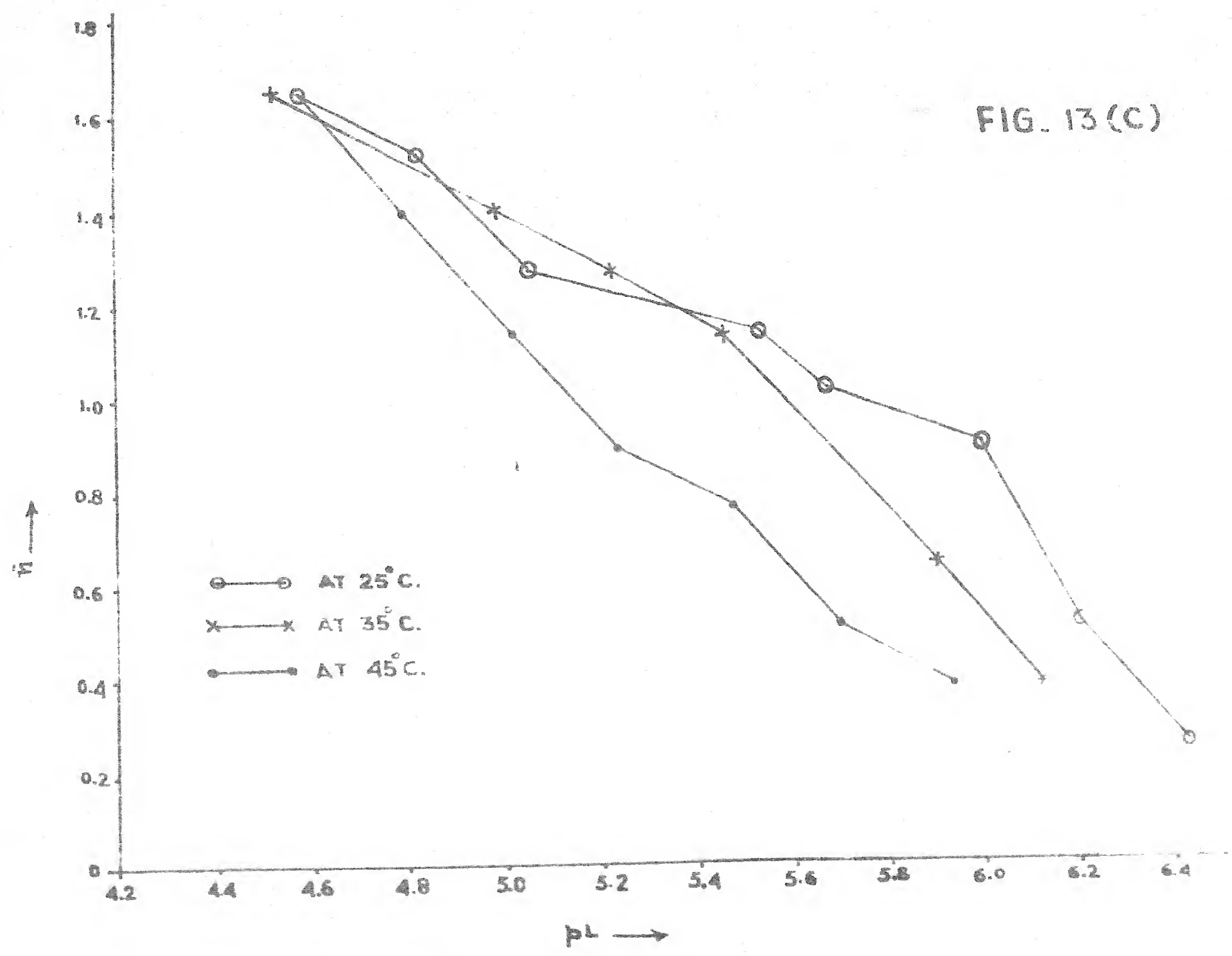


FIG. 13 (b)



1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$\bar{n}$
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
pL
AT 25°C.
AT 35°C.
AT 45°C.



1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
n̄ →
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
pL →
AT 25°C.
AT 35°C.
AT 45°C.

FIG. 13 (C)

FIG. 13(d)

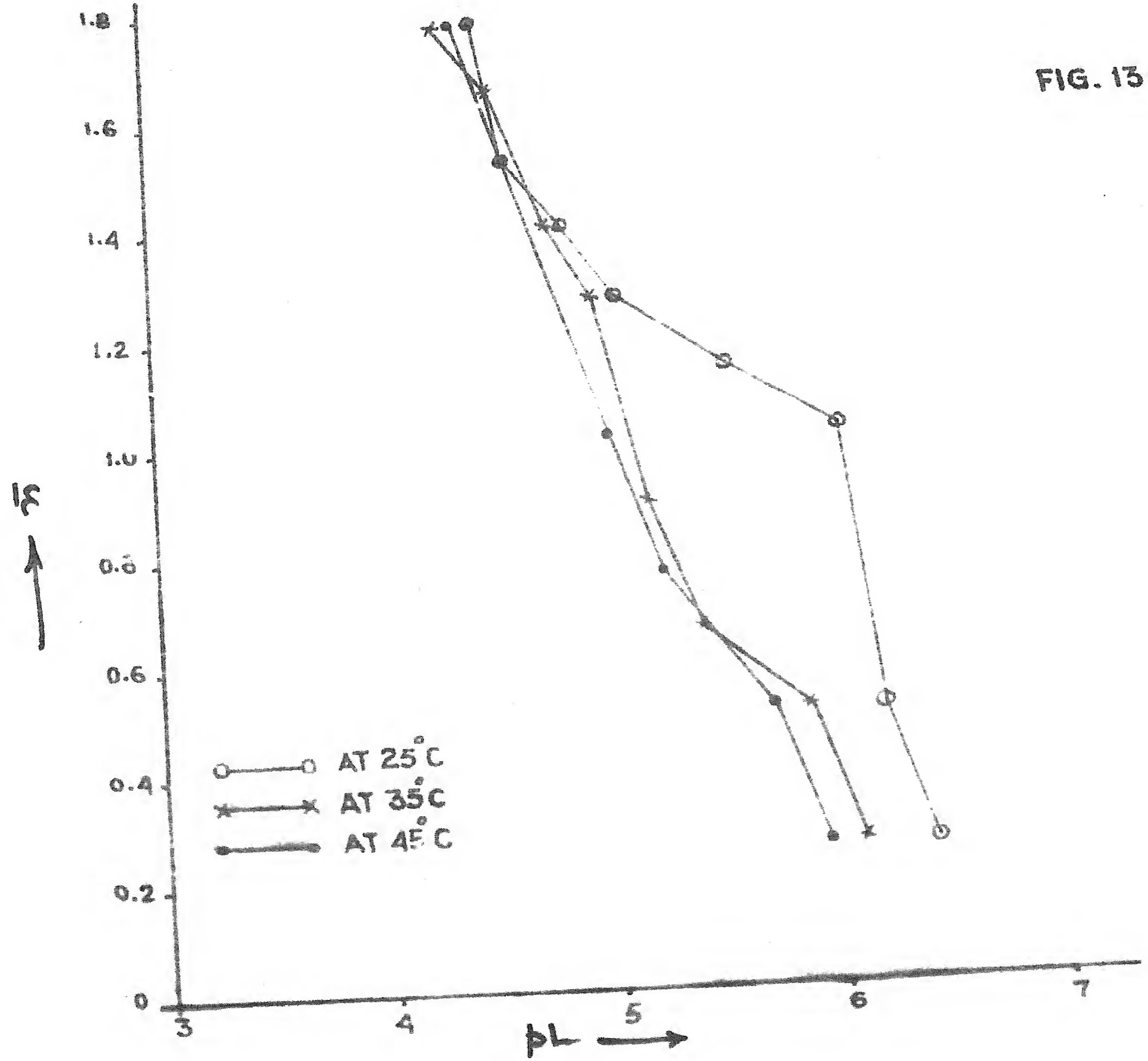
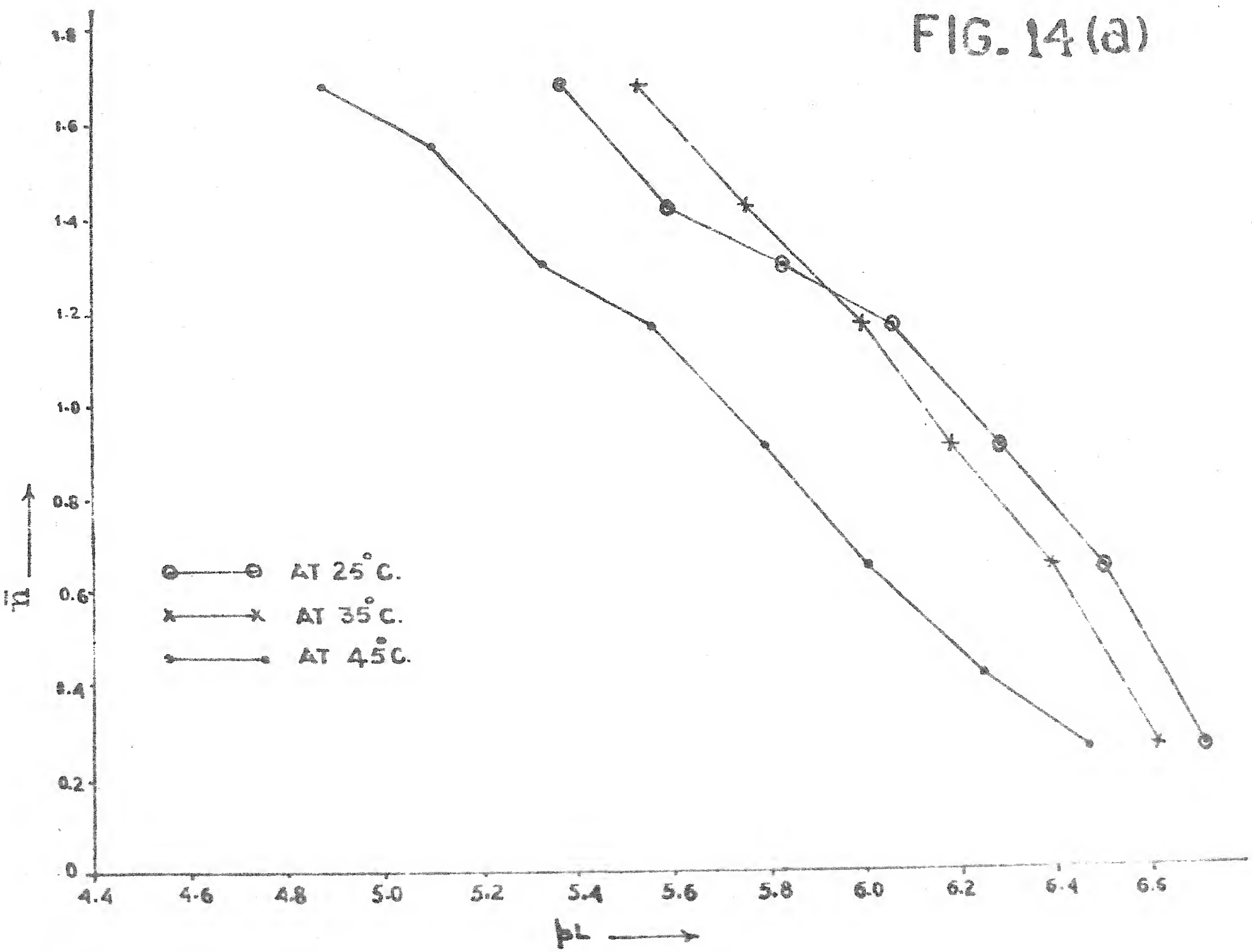
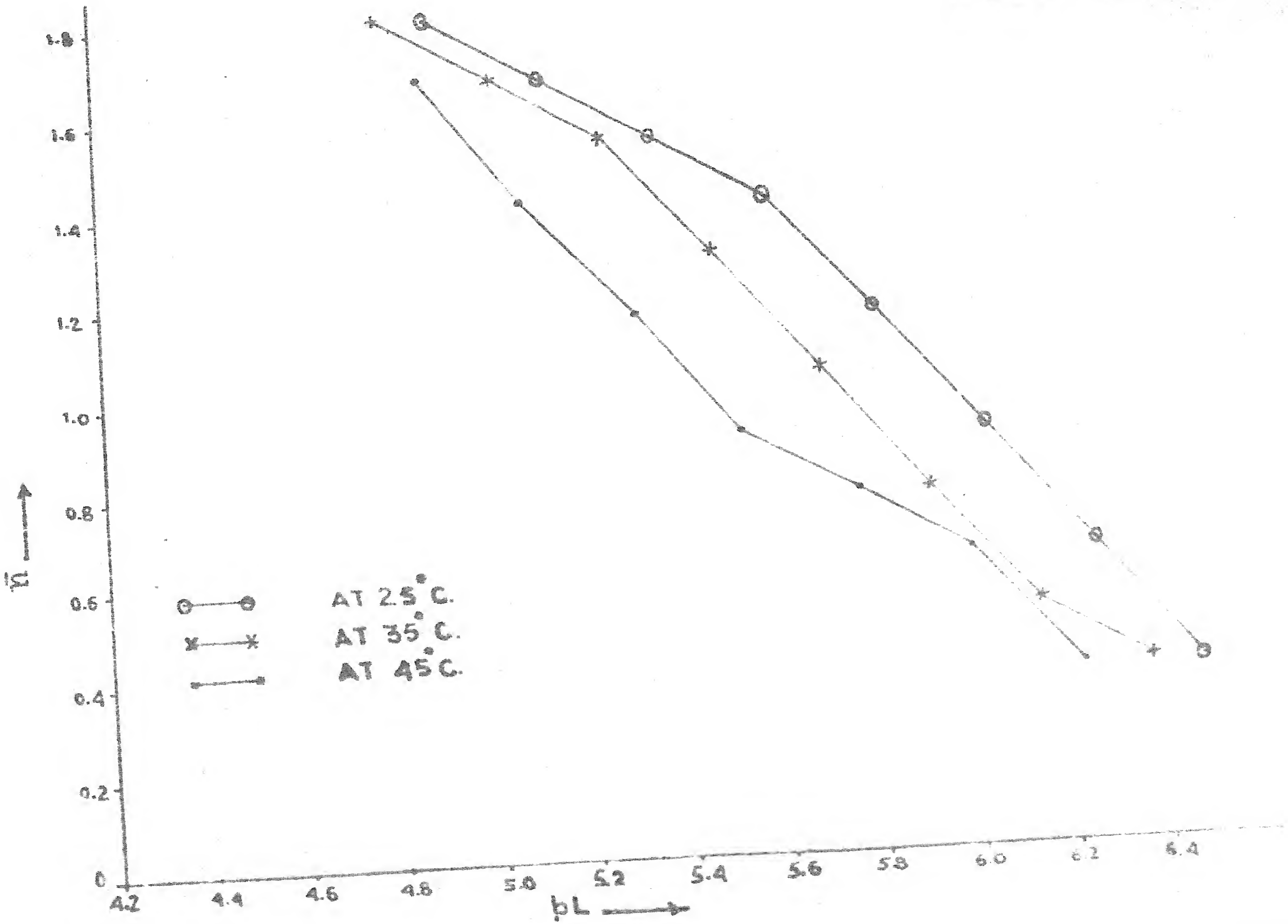


FIG. 14 (a)



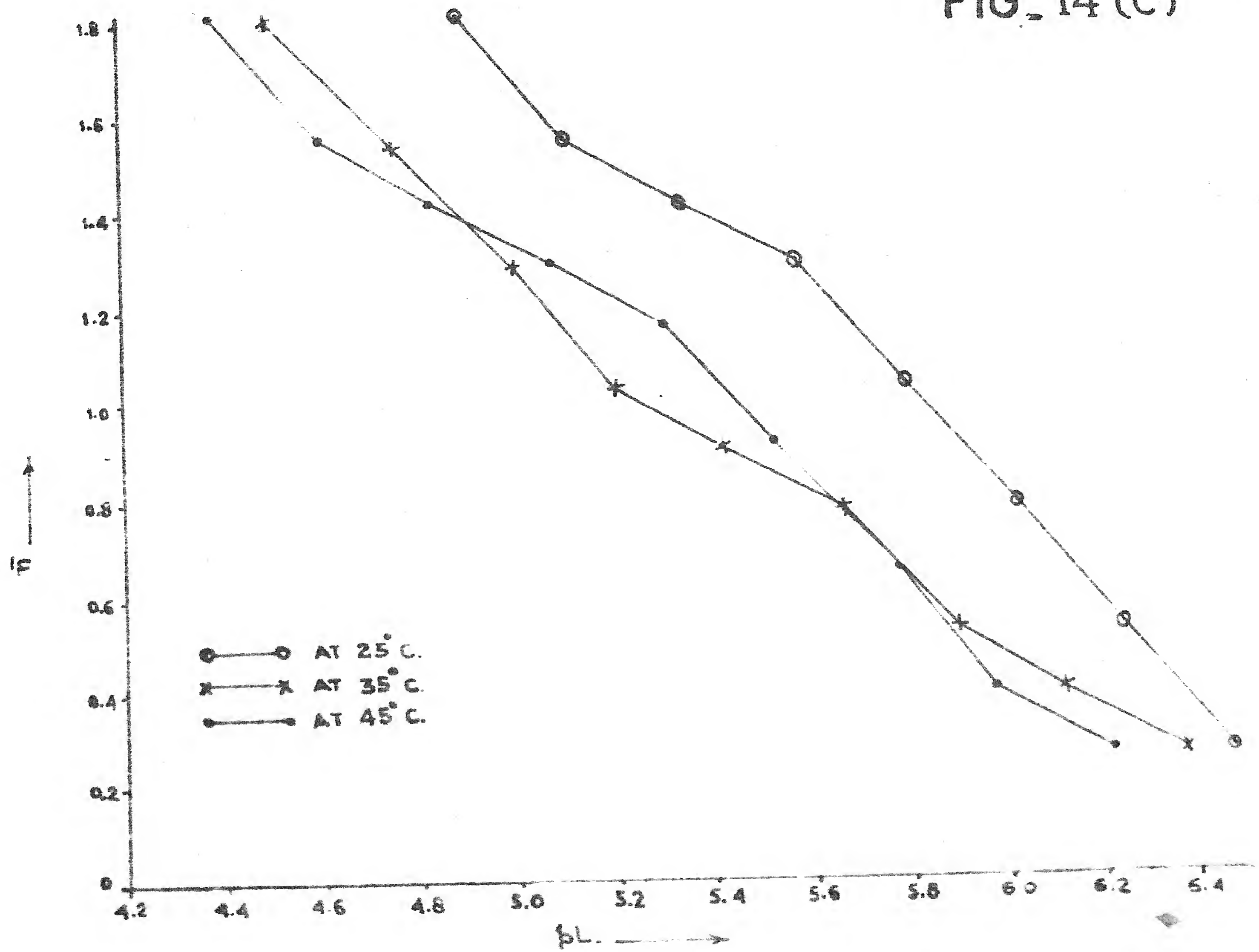
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$\bar{n}$
AT 25°C.
AT 35°C.
AT 45°C.
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.5
pL

FIG. 14 (b)



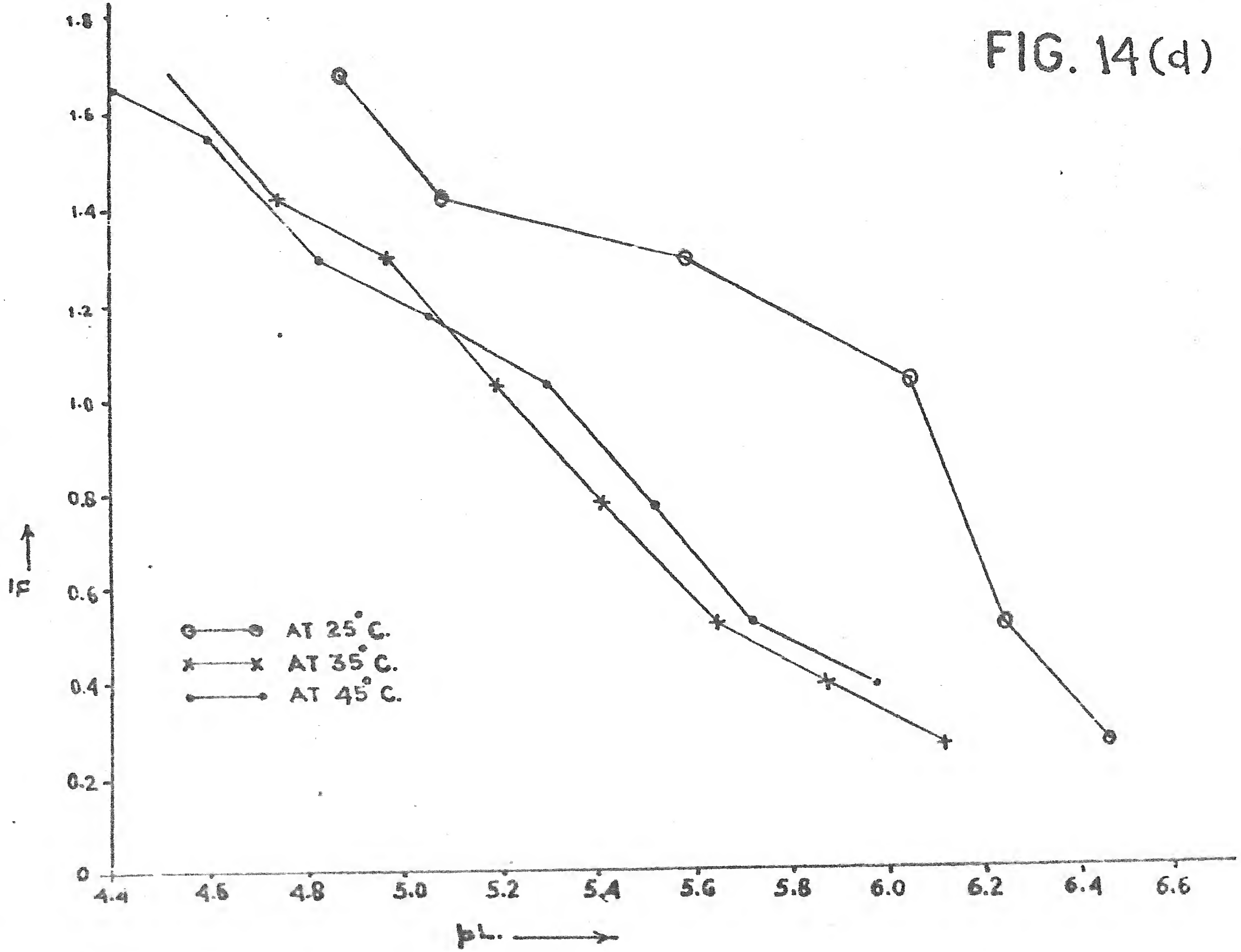
AT 25°C.
AT 35°C.
AT 45°C.
$\bar{n}$
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
pL

FIG. 14 (C)



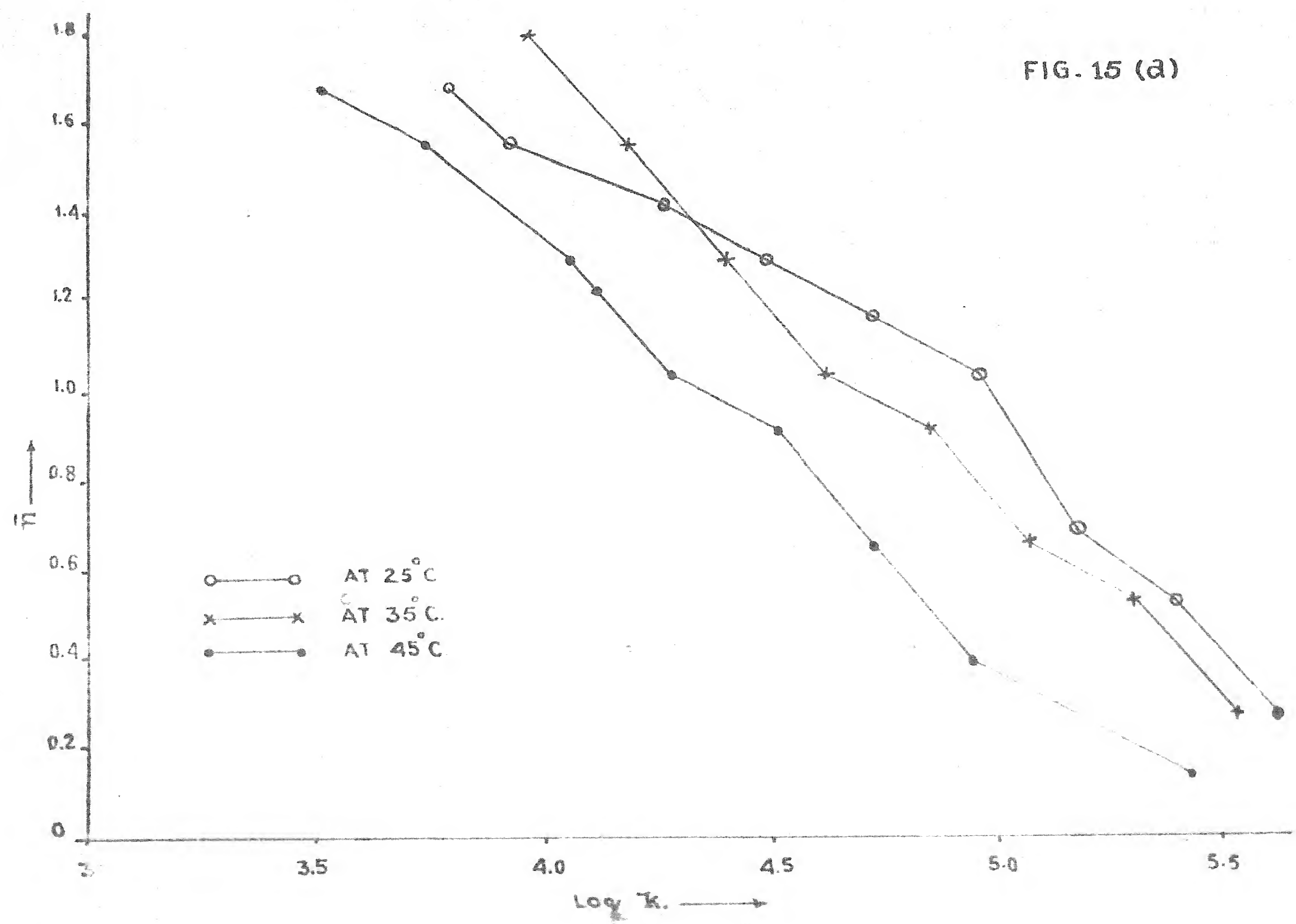
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
pL.
AT 25° C.
AT 35° C.
AT 45° C.

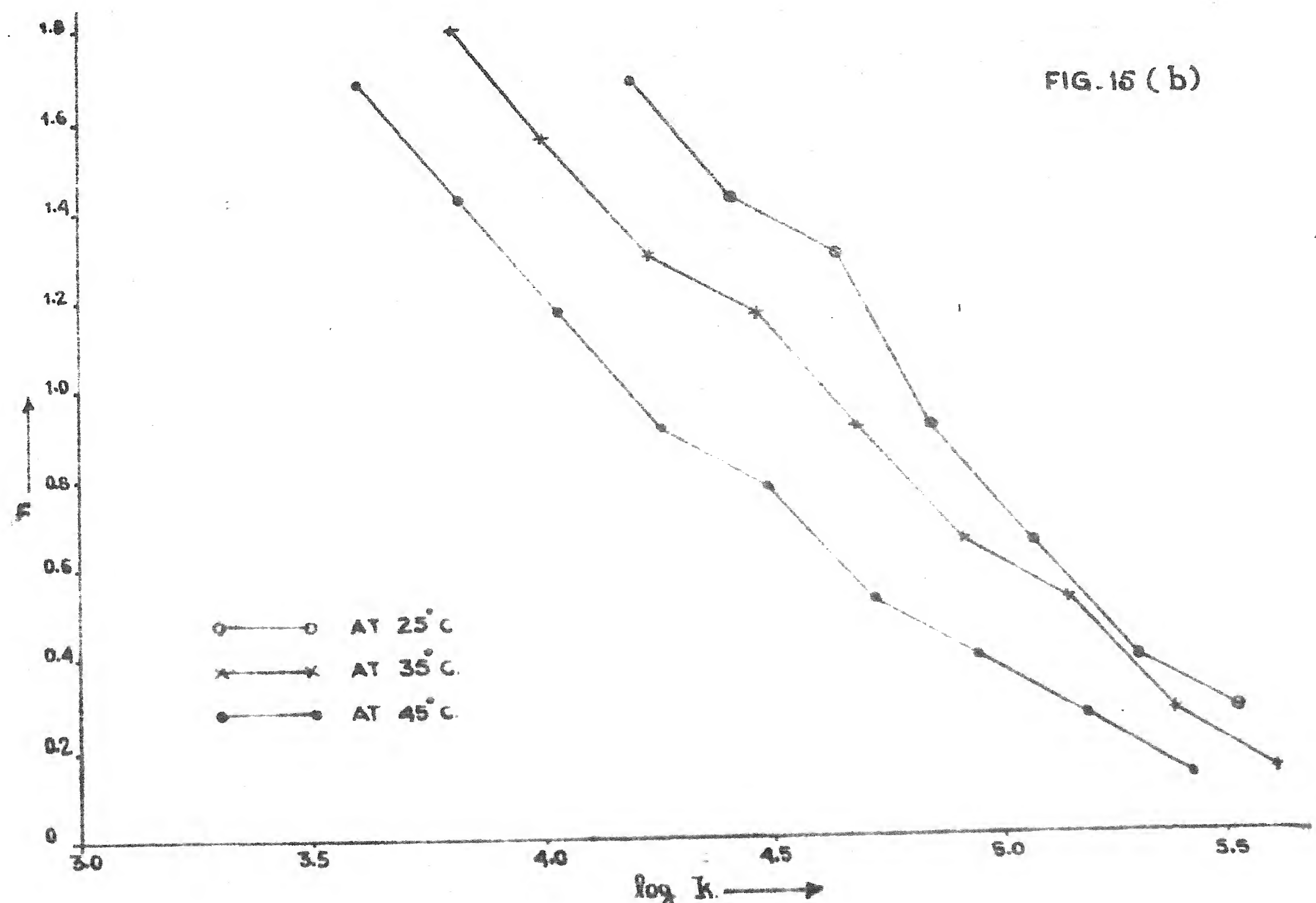
FIG. 14(d)



1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
IF
AT 25°C.
AT 35°C.
AT 45°C.
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
pL.

FIG. 15 (a)

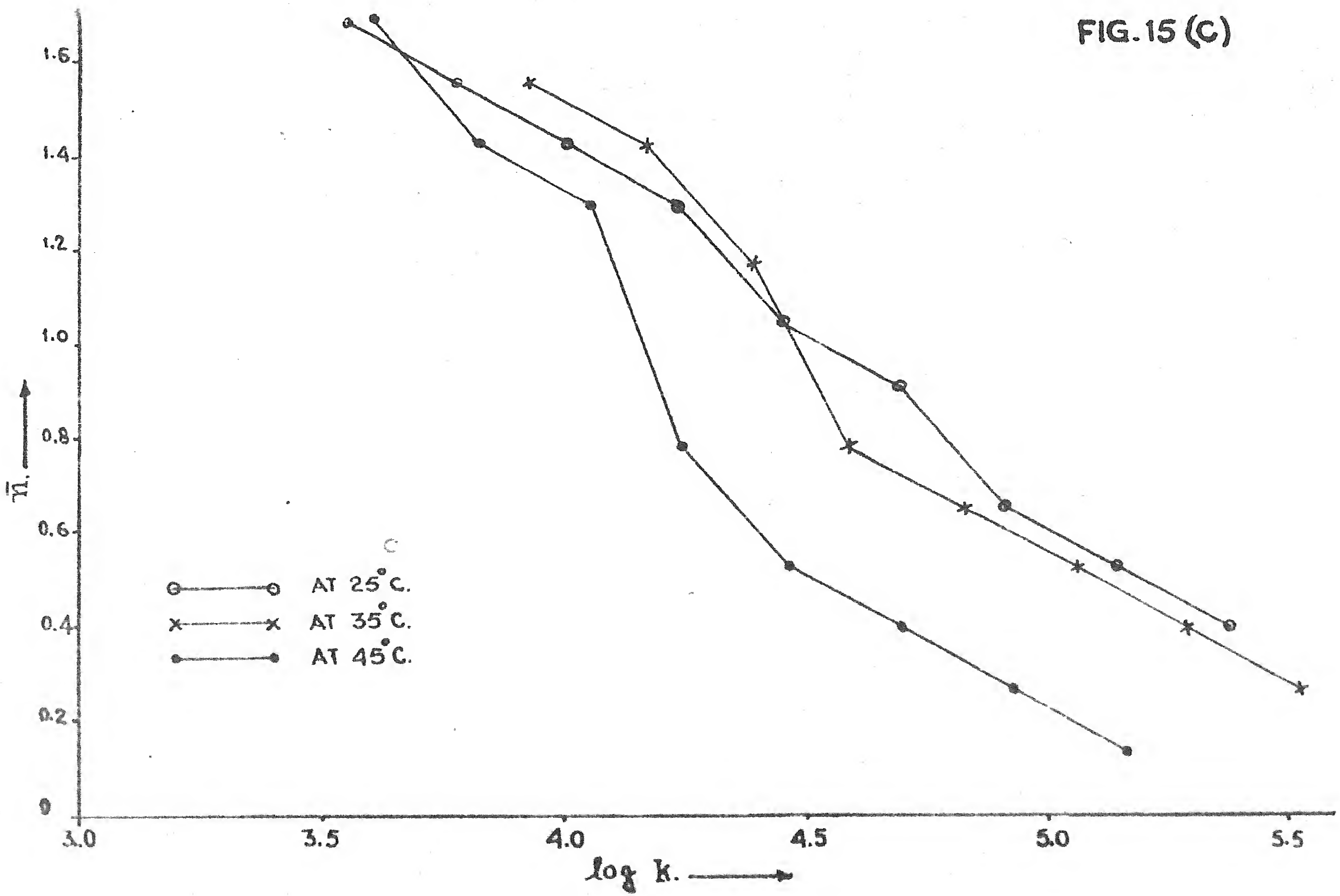

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$\bar{n}$
AT 25°C
AT 35°C
AT 45°C
3.5
4.0
4.5
5.0
5.5
Log K.



1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
F
3.0
3.5
4.0
4.5
5.0
5.5
log k
AT 25° C
AT 35° C.
AT 45° C.

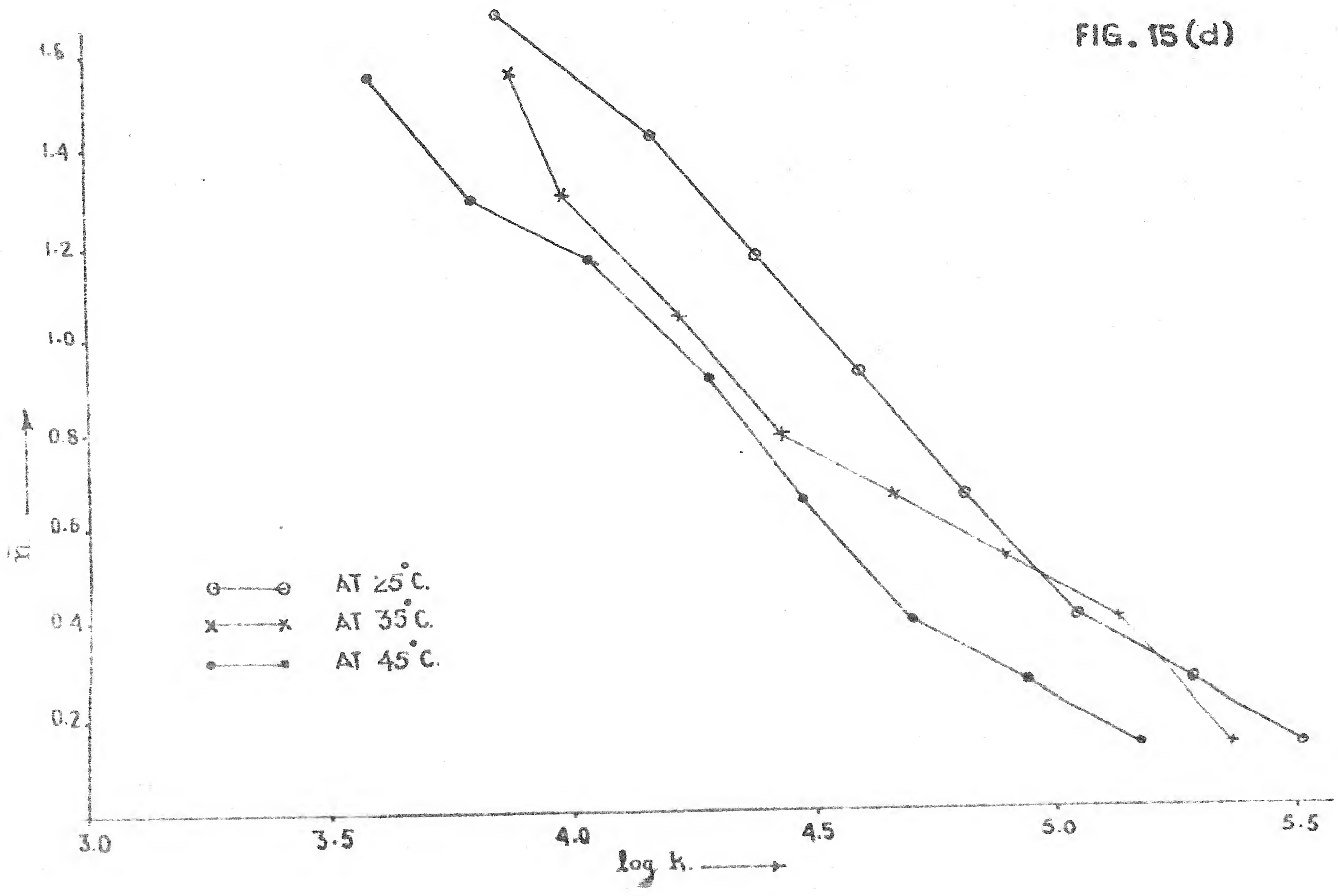
FIG. 15 (b)

FIG. 15 (C)



1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$\bar{n}$
3.0
3.5
4.0
4.5
5.0
5.5
log k.
AT 25°C.
AT 35°C.
AT 45°C.

FIG. 15 (d)


1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
$\bar{n}$
AT 25°C.
AT 35°C.
AT 45°C.
3.0
3.5
4.0
4.5
5.0
5.5
log k.

C H A P T E R - VI.

Discussion.

CHAPTER VI

DISCUSSION:

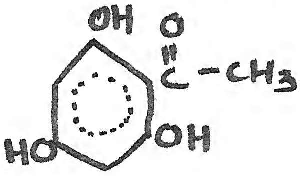
In this chapter the results obtained in the previous chapter (Chapter V) have been taken for discussion; so that some concealed aspects of dielectric constant (solvent) and change of temperature on complexation with metal ions by complexing agent can be made. In this chapter an attempt has also been made to discuss the variation in the stability constants of the metals. The discussion in this chapter is subdivided as follows:

1. Proton-ligand stability constant in different solvents:

As it has already been discussed that the curves for the Set II (ligand) show the maximum possibility of the H^+ ions, which may dissociated from the ligand. In the present investigation the ligand (phloroacetophenone, abbreviated as PAP) show only one point of inflection in all the solvents and at different temperatures (figs. 1 (a,b,c) to 5 (a,b,c) . Therefore, there is only one dissociable H^+ ion in the ligand. R.C. Agarwal[1] has also found that, there is only one dissociable H^+ possible in PAP in 75% dioxane - H_2O

system at 25°C.

It is abvious from the structure of the PAP that, there is possibility of three dissociable H^+ ions. The abnormality in the H^+ ion dissociation clearly indicates that the position of hydroxy groups (-OH) in the ligand have stronger influence. In PAP the three hydroxy groups are attached at position no. 2, 4 and 6 as follows:



PAP

It is shown by R.C. Agarwal[2] that only hydroxy groups at ortho an meta positions are dissociated. In the PAP the hydroxy group is situated at ortho position, hence, there is only one dissociable H^+ ion which is obtained in this ligand. Thus, the value of 'Y' is kept equal to one at the time of calculation of proton-ligand stability constant of PAP.

From the table 26, it is seen that proton-ligand stability constant of PAP in different solvents (50% solvent $-H_2O$ mixture) have the following relation:

	Acetonitrile	<	Methanol	<	Ethanol	<	Iso-propanol	≤	DMF
at 25°C	7.99	<	8.01	<	8.31	<	8.39	<	8.42
at 35°C	7.89	<	7.98	<	8.295	<	8.32	≤	8.32
at 45°C	7.83	<	7.94	<	8.065	<	8.13	<	8.17

The following is the relationship between dielectric constant of the solvents:[5]

DMF > Acetonitrile > Methanol > Ethanol > Iso-propanol

109.5 > 37.5 > 32.6 > 24.3 > 18.3

R.S. Saxena etal[6], studied the proton-ligand stability constant of Dl- tryptophan in 20% DMF, Iso-propanol and Acetonitrile -water system and obtained the following results.

DMF > Iso-propanol > Acetonitrile

(9.24) > (9.14) > (9.08)

The dielectric constant of the solvents depends on viscosity[7] and stability constant on ionic interaction in solution[8]. The solvents which have higher dielectric constant are better solvents[9]. The molecular solubility relationship as suggested by Walden is as follows:

$$K = \frac{D}{\sqrt[3]{S}}$$

$$\text{and} \quad S = \frac{100\, n_b}{n_a + n_b}$$

where, $D \longrightarrow$ dielectric constant

$S \longrightarrow$ molecular solubility

$K \longrightarrow$ constant

$n_a \longrightarrow$ moles of solute

$n_b \longrightarrow$ moles of solvent

As already discussed that the dielectric constant of the solvents depend on viscosity and the viscosity depends on temperature.

On rising the temperature the viscosity of the solvents decreases and hence the dielectric constant increases. On going through the results given in table 26 and already discussed earlier that the less, the dielectric constant higher is the proton-ligand stability constant of the ligand. In the present investigation this criteria is shown by all the solvents except DMF. DMF has the highest dielectric constant than all other solvents. As such the proton-ligand stability constant of PAP in DMF system should be the lowest but, here, the values obtained are the highest. The highest values in DMF system are probably due to the nature of the solvent i.e. it is as good solvent as water

(dielectric constant of water is 81).

Due to rise of temperature the dielectric constant of the solvent increases i.e. the dielectric constant of the solvents at 25°C, 35°C and 45°C will increase with temperature. When the dielectric constant will be higher the proton-ligand stability constant of the PAP will be lower. It is further obvious from the table 26, that the proton-ligand stability constant of PAP in all the solvents decreases with rise of temperature.

In the present investigation the calculation were made by half $\bar{n}_A$ method and probability of error is $\pm$ 0.03.

2. Metal-ligand stability constant of the complexes different solvents:

The metal-ligand stability constant logk or pL of the metal complexes are calculated with the help of curves from Set II (ligand curve) and Set III, Set IV, Set V and Set VI (metal curves) (Figs. 1 (a,b,c) to 5 (a,b,c), by the half $\bar{n}$ method. The values of the metal-ligand stability constant, pL with PAP in different solvents and temperatures are reported in the table 27.

The interaction of metal ions with the ligand in the present study takes place stepwise i.e. 1:1 and 1:2 therefore, two values of the stability constants are obtained with all the metal - PAP complexes. The overall stability constant of the complex is obtained by the following formula.

$$\log \beta = \log k_1 + \log k_2$$

On going through the results quoted in the table 27 have the following relationships. (All the results quoted are in 50% solvent $-H_2O$ system).

Cu(II) -PAP complex:

	Acetonitrile		Methanol		Ethanol		Iso-propanol		DMF
	Acetonitrile	$<$	Methanol	$<$	Ethanol	$<$	Iso-propanol	$\leq$	DMF
at 25°C	9.70	$<$	10.10	$<$	11.30	$<$	12.40	$\approx$	12.10
at 35°C	9.60	$\approx$	9.60	$<$	10.50	$<$	12.00	$\approx$	12.00
at 45°C	8.50	$<$	9.55	$<$	9.95	$<$	11.30	$\approx$	11.30

Ni(II) -PAP complex:

	Acetonitrile	$<$	Methanol	$<$	Ethanol	$<$	Iso-propanol	$\leq$	DMF
at 25°C	9.50	$<$	9.85	$<$	10.95	$<$	11.55	$<$	11.82
at 35°C	9.40	$\approx$	9.40	$<$	10.00	$<$	11.20	$<$	11.46
at 45°C	8.72	$<$	9.20	$<$	9.90	$<$	10.80	$<$	11.13

<u>Co(II)-PAP complex:</u>

	Acetonitrile		Methanol		Ethanol		Iso-propanol		DMF
	Acetonitrile	$<$	Methanol	$<$	Ethanol	$<$	Iso-propanol	$\leq$	DMF
at 25°C	9.25	$<$	9.60	$<$	10.70	$<$	11.05	$<$	11.45
at 35°C	9.15	$\simeq$	8.95	$<$	9.75	$<$	10.80	$\simeq$	10.70
at 45°C	8.30	$<$	8.35	$<$	9.45	$<$	10.40	$<$	10.50

<u>Fe(II)-PAP complex:</u>

	Acetonitrile		Methanol		Ethanol		Iso-propanol		DMF
	Acetonitrile	$<$	Methanol	$<$	Ethanol	$<$	Iso-propanol	$\leq$	DMF
at 25°C	8.90	$<$	9.20	$<$	10.20	$<$	10.90	$<$	11.30
at 35°C	8.80	$<$	8.90	$<$	9.525	$<$	10.55	$<$	11.35
at 45°C	8.15	$\simeq$	8.15	$<$	8.75	$<$	10.30	$\simeq$	10.25

It can be concluded from the aforesaid results that overall stability constants (log β) of the complexes show the similar trend as the proton-ligand stability constant, i.e. less the dielectric constant higher is the metal-ligand stability constant. Further, as the dielectric constant increases with the rise of temperature (25°C, 35°C, 45°C), the metal-ligand stability constant decreases.

It is also apperant from the table 27, that metal-ligand stability constants of Cu(II), Ni(II), Co(II) and Fe(II)

in all the solvent $-H_2O$ mixture and different temperatures have the following relationship.

		Cu(II)	>	Ni(II)	>	Co(II)	>	Fe(II)
<u>Methanol-H_2O:</u>	at 25°C	10.10	>	9.85	>	9.60	>	9.20
	at 35°C	9.60	>	9.40	>	8.95	>	8.90
	at 45°C	9.55	>	9.20	>	8.35	>	8.15
<u>Ethanol-H_2O:</u>	at 25°C	11.30	>	10.95	>	10.70	>	10.20
	at 35°C	10.50	>	10.00	>	9.75	>	9.525
	at 45°C	9.95	>	9.90	>	9.45	>	8.75
<u>Iso-propanol-H_2O:</u>	at 25°C	12.40	>	11.55	>	11.05	>	10.90
	at 35°C	12.00	>	11.20	>	10.80	>	10.55
	at 45°C	11.30	>	10.80	>	10.40	>	10.30
<u>DMF $-H_2O$:</u>	at 25°C	12.10	>	11.82	>	11.45	>	11.30
	at 35°C	12.00	>	11.45	>	10.70	>	10.35
	at 45°C	11.30	>	11.13	>	10.50	>	10.25

As the change in free energy (ΔG) is directly co-related with the stability constant, analogous relationships are obtained (Table 28 (a) . The overall stability constant ($\log \beta$) and change in free energy (ΔG) of the complexes follow the well established Irving - Williams Rule[10,11].

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C H A P T E R - VII.

Summery and Conclusion.

CHAPTER VII

SUMMARY AND CONCLUSIONS:

As have been discussed in the beginning (Chapter I) that transition metals of 'd' sub-shells are more reactive then the inner transition metals i.e. lanthanide. Therefore, interaction of metals of 'd' sub-shells with the ligands in solution state is more convenietly studies.

In Chapter I of this thesis the extensive survey of literature on the Cu(II), Ni(II), Co(II) and Fe(II) complexes and their chemistry have been complted with object and intention of the present investigations. In Chapter II, III and IV the methods of determination of the presence of complexation, preparation of ligand and actual procedure for experimentation, have been discussed, respectively. On the basis of the studies made by several other workers the pH-meteric method has been choosen for the present studies. The mediums of interaction for metal-ligand complexation have been selected on the basis of dielectric constants.

In Chapter V, the results are evaluated from the experimental data of Chapter IV. At the time of evaluation of the results all the necessary attention and aspects have been

considered before final discussion of the results. In Chapter VI, the results obtained in Chapter V have been taken for discussion. In this chapter, it is observed that viscosity of the solvents i.e., dielectric constant has significant role and the effect is clearly observed during present investigations. It is also observed that if the dielectric constant of the medium are varied by rise of temperature than to annul this effect the stability constant decreases.

The metal-ligand stability constant of the metals in different solvents and at different temperature shows the well established Irving-Williams Rule i.e.,

$$Cu(II) > Ni(II) > Co(II) > Fe(II).$$

A P P E N D I X

1. List of papers published, accepted and communicated.
2. Re-prints of Published Papers.

List of papers published, accepted and communicated.

1. Stability constants and thermodynamic functions of Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) chelates with Glutamic acid.

   R.C. Agarwal & S.L. Agarwal,

   Thermochimica Acta, 44, 121-123 (1981)

2. Fe(II), Co(II), Ni(II) and Cu(II) chelates with Phloro-acetophenone in 50% Ethanol -H_2O.

   R.C. Agarwal & S.L. Agarwal,

   Thermochimica Acta, 47, 99-103 (1981)

3. Thermodynamic functions of some transition metal/chelates with phloroacetophenone in 50% Methanol -H_2O.

   R.C. Agarwal & S.L. Agarwal,

   Thermochimica Acta, 52, 371-374 (1982)

4. Effect of Dielectric Constant on Stability Constants of the complexes.

   R.C. Agarwal & S.L. Agarwal,

   J. Thermal Analysis.

5. Effect of temperature and dielectric constant on complexation.

   R.C. Agarwal & S.L. Agarwal,

   (Communicated)